Tetrahedron Vol 39, No 23, pp. 3845 to 3879, 1983
Printed in Great Britain

0040 4020/83 $5.00 + 00
Pergamon Press Ltd.

TETRAHEDRON REPORT NUMBER 156

THE PHOTOCHEMISTRY OF IMINIUM SALTS AND RELATED HETEROAROMATIC SYSTEMS

PATRICK S. MARIANO
Department of Chemistry, University of Maryland, College Park, MD 20742, U.S.A.

(*Received in the USA* 16 *November* 1982)

CONTENTS

INTRODUCTION

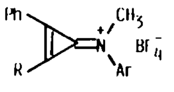
The past decade has seen a renewed interest in the photochemistry of compounds containing nitrogen in a variety of chromophoric systems. The extensive work on the excited state chemistry of imines has been thoroughly reviewed[1,2] as have the photoreactions of molecular arrays having the $R_2C{=}NR$ grouping as part of aromatic rings. Receiving perhaps more intensive investigation in recent years is the area of iminium salt ($R_2C{=}\overset{+}{N}R_2$) and related N-heteroaromatic salt photochemistry. The rising interest in this topic has paralleled the increasing concern with electron transfer pathways for excited state deactivation and reaction coupled with the rapidly growing number of applications of ground state iminium salt cyclization processes in heterocycle and natural product synthesis. The purpose of this report is to review the general area of iminium salt photochemistry and in doing so to attempt to place both the photophysical and photochemical properties of these systems into a unified and hopefully understandable framework.

In the initial sections of the report, some of the characteristic ground and excited state properties of compounds containing the iminium cation grouping will be briefly surveyed in order to establish a background for a thorough analysis of excited state chemical phenomena. Since the photochemistry of these systems appears to be dominated by pathways in which the electron deficient iminium salt ground and excited states serve as acceptors in one electron transfer processes, we will also outline some of the basic principles of photochemical electron transfer. This will be useful in later discussions where excited state quenching and reaction processes are reviewed.

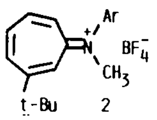
CHARACTERISTICS OF THE IMINIUM CATION CHROMOPHORE

Several excellent, comprehensive reviews summarizing structural, spectroscopic and chemical properties of a wide variety of iminium salts have been written.[3] For the purposes of this report it will be sufficient to present preliminary information which focuses on the electronic characteristics of the ground and excited states of the iminium cation ($R_2C{=}\overset{+}{N}R_2$) chromophores. Molecular orbital calculations and spectroscopic data for these systems combine to support the generalized view that the $R_2C{=}\overset{+}{N}R_2$ valence bond representation of α-aminocarbenium ions is more illustrative of the properties of this cation. This structure with a full π-bond between carbon and nitrogen and a full positive charge on nitrogen is isoelectronic with simple olefins and is in full accord with calculated and observed large ground state C–N rotational barriers for the simple, alkyl substituted systems. MO calculations by Kollman on the parent methyleniminium cation ($H_2\overset{+}{N}{=}CH_2$) suggest that rotational barriers corresponding to transformation of planar to 90°-twisted geometries fall in the range of 70–90 kcal mol^{-1}.[4,5] The comparatively lower value of 57 kcal mol^{-1} calculated for syn-anti isomerization of the corresponding imine, $H_2C{=}NH$ is expected since, unlike the iminium salt case, isomerization by nitrogen inversion is possible here.[5]

Nuclear magnetic resonance analysis by Olah[7] and McDanogh[8] with a series of protonated alkyl and aryl substituted aldimines and ketimines have provided strong evidence for the existence of these substances in configurationally static, planar structures. Rotational barriers in these systems can be lowered by locating the iminium salt carbon in ring systems capable of efficient positive charge stabilization. This is exemplified by the low C=N bond rotational barriers of 24 and 16 kcal mol^{-1} observed for the respective cyclopropenylidene[9] and cycloheptatrienylidene[10] salts **1** and **2**.

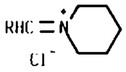


1

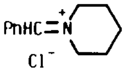


2

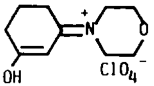
The correspondence between electronic characteristics of iminium cations and olefins is also reflected in UV spectroscopic properties. Only $\pi-\pi^*$ transitions are possible for the iminium cation chromophore and these occur in wavelength regions of the UV and visible spectra similar to those for olefin analogs. Several of the many examples demonstrating this point are present in the simple alkyl substituted, C-phenyl conjugated, and hydroxyvinyl substituted iminium salts 3–5 which display absorption maxima at 222 (CH_3CH),[11] 275 (EtOH),[12] and 317 nm (EtOH),[13] respectively.



3



4



5

The $\pi-\pi^*$ transitions of N-heteroaromatic salts which have the $R_2C{=}NR_2$ grouping within cyclic conjugated systems likewise occur in regions similar to those for their aromatic hydrocarbon counterparts (see Table 1). Iminium salts and hydrocarbon analogs display other similarities in their photophysical properties. Phenyl-conjugated and N-heteroaromatic iminium salts have modestly long lived singlet excited states and undergo efficient conversion to ground states by light emission. Characteristic photophysical data for representative salts and all carbon relatives are accumulated in Table 1.

A major difference in ground and excited state chemical properties of olefins and iminium salts results from the presence of the delocalized positive charge in the latter substances. Indeed, the molecular orbital calculations alluded to above[4-5] demonstrate that both HOMO and LUMO π-orbitals of the methyleniminium cation fall at much lower energies than those of ethylene (Fig. 1). Furthermore, the MO wavefunctions for $H_2C{=}\overset{+}{N}H_2$, pictorially depicted in Fig. 1, reflect the relative electronegativity of C and N atoms and are in accordance with ground and excited state chemical properties of compounds containing this chromophore. The typical ground state transformations of iminium salts summarized in Scheme 1, which include nucleophilic attack on carbon and deprotonations from nitrogen or carbons on or flanking the cationic grouping, can be understood in terms of valance bond or molecular orbital methodologies.[3]

The presence of low lying LUMOs in iminium salts enables these species to undergo ready one

Table 1. Characteristic photophysical data for selected iminium salts and hydrocarbon analogs[14]

Compound	ϕ_f	τ_f (ns)	$\Delta E_{0,0}^{S_1}$ c (kcal/mol)	λmax Emission (nm)	λmax Absor. (nm)
2-phenyl-1-pyrrolinium ClO_4^-	0.16	16	89	375	264
1-methyl-2-phenyl-1-pyrrolinium ClO_4^-	0.07	1	-	-	258
1-phenylcyclopentene	0.72^d	14^d	-	-	-
styrene	-	11^a	98^a	370^b	250^b
quinolinium ClO_4^-	0.88	12	80	414	312
isoquinolinium ClO_4^-	0.94	23	82	376	336
naphthalene	0.20^a	100^a	92^a	321^b	376^b
1-methylquinolinium ClO_4^-	0.85	13	82	402	315
1-methylnaphthalene	0.21^a	67^a	90^a	339^b	282^b
2-methylisoquinolinium ClO_4^-	0.94	25	81	380	334
2-methylnaphthalene	0.27^a	59^a	90^a	335^b	277^b

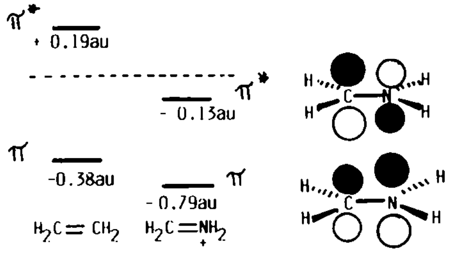
a) Reference 15

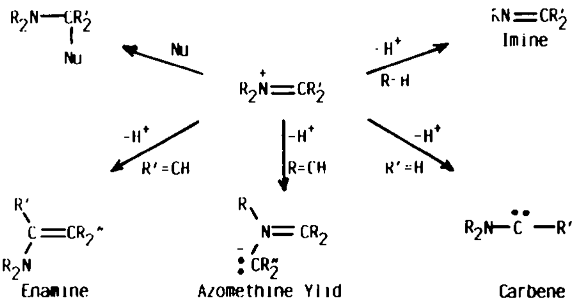
b) Reference 16

c) Singlet excited state energy

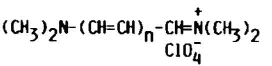
d) Reference 17

electron reduction resulting in formation of stabilized[18] α-amino radicals. Studies by Arnold *et al.* of vinylogous polymethinium salt (**6**) polarographic reductions demonstrate that the half wave reduction potentials ($E_{1/2}(-)$) shift to more positive values with increasing chain length.[19] The constancy of the change indicates a good correlation between $E_{1/2}(-)$ and LUMO energies which experience a regular decrease with increasing conjugation. Further evidence linking LUMO energies to $E_{1/2}(-)$ has been gained[19] for a series of *p*-substituted-phenyl cyanine dyes **7** and **8** for which excellent linear relationships between $E_{1/2}(-)$ and Hammett σ_p constants exists.



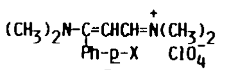


Scheme 1.



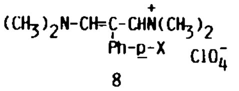
$(CH_3)_2N\text{-}(CH{=}CH)_n\text{-}CH{=}\overset{+}{N}(CH_3)_2\ ClO_4^-$

6



$(CH_3)_2N\text{-}\underset{Ph\text{-}p\text{-}X}{C}{=}CHCH{=}\overset{+}{N}(CH_3)_2\ ClO_4^-$

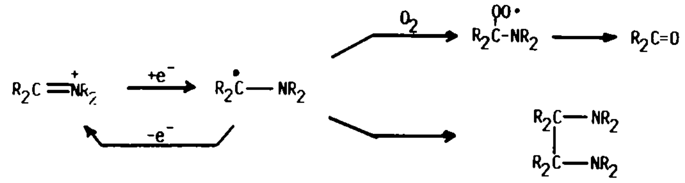
7



$(CH_3)_2N\text{-}CH{=}\underset{Ph\text{-}p\text{-}X}{C}\text{-}CH\overset{+}{N}(CH_3)_2\ ClO_4^-$

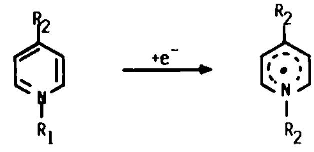
8

The chemical features of iminium salt polarographic reductions have been thoroughly explored by Andrieux and Saveant. A variety of simple alkyl and aryl substituted iminium perchlorates have been shown to undergo single electron reduction in organic solvents such as acetonitrile and DMF with half wave potentials ($E_{1/2}(\text{-})$) in the range of -1.95 to -0.84 volts. In several cases where conjugating substituents are present on carbon, the α-amino radicals are formed reversibly in the electrochemical process and possess sufficiently long lifetimes (*ca* 100 ms) to be detected by ESR-spectroscopy.[20] When formed under aerobic conditions, the α-amino radicals react with oxygen to produce carbonyl products by the pathway shown in Scheme 2. The electrochemically generated radicals lacking radical stabilizing groups undergo rapid dimerization to produce vicinal diamines (Scheme 2).[20a,21,22]



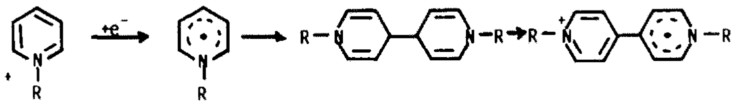
Scheme 2.

The electron deficiency of the iminium salt grouping serves as a major control of the ground state chemistry of N-heteroaromatic cations. Among the interesting properties of these systems is their ready participation as acceptors in electrochemical or metal induced one electron transfer processes. For example, the 1-hydropyridinyl radicals **10** can be formed by zinc metal reduction of the corresponding pyridinium salts[23] and are sufficiently long-lived to be detected by ESR-spectroscopic methods.[24] Perhaps the most interesting examples of the 1-hydropyridinyl radicals are those produced by zinc or sodium amalgam reduction of 1-alkyl-4-electron withdrawing substituted pyridinium salts **11**.[25] Surprisingly, electron transfer appears to occur even when the salts are exposed to strongly basic conditions in alcohol or DMSO solvent.[26] The extreme persistance of radicals of general structure **12** under anaerobic conditions has been attributed to merostabilization arising by simultaneous substitution of π-donating and withdrawing substituents on centers bearing high odd electron densities.[27] When substituents at the C-4 position are absent, the 1-alkylpyridinylradicals undergo rapid dimerization as exemplified by the efficient transformation of pyridinium salts **13** to the corresponding dialkylviologen cation radicals **15** via the 4,4-dimers **14**.[28] Numerous additional studies of one electron reductions of pyridinium salts have been conducted.[29-34]



9 ($R_1{=}R_2{=}H$)
11 (R_1=alkyl, $R_2{=}CO_2R$ or CN)

10
11



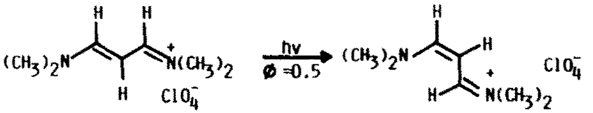
13 14 15

EXCITED STATE PROPERTIES OF IMINIUM SALTS

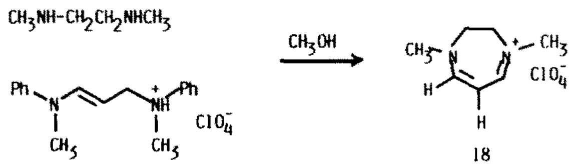
Predictions about the excited state properties of compounds possessing the iminium cation chromophore can be made on the basis of the wealth of information on the photochemical characteristics of their all carbon, isoelectronic counterparts and by using molecular orbital treatments which evaluate excited state electron densities, π-bond orders, and electrochemical potentials. For example, a view of the MO features of this chromophore summarized in Fig. 1 suggests that the $\pi-\pi^*$ excited states would have reduced C=N π- bond orders due to the population of antibonding orbitals. Thus, the prohibitively larger barrier to EZ isomerization found in the ground states would be missing in the excited state manifold. Other types of photoreactions typically followed by conjugated unsaturated hydrocarbons, including electrocyclic ring closure or opening, and cycloadditions, should be available to substances containing the iminium salt grouping. It is important to note that $\pi-\pi^*$ excitation is expected to produce an excited state with greater electron density on carbon of the iminium cation chromophore than in the ground state. Accordingly, nucleophilic additions by classical dipolar mechanisms should not be characteristic of iminium salt photochemistry.

EZ-Isomerizations, electrocyclizations and cycloadditions

The results of numerous studies suggest that strong analogies exist between the excited state chemistry of olefins and iminium salts. Earlier investigations by Schiebe *et al.*[35] and others[36] have shown that polymethiniminium salts (e.g. **16**) undergo photochemical C=C *trans–cis* isomerization upon irradiation. The initial postulate by Hoppe and Baumgartner[37] that irradiation transforms the stable *trans*-cyanine dye **16** to its *cis*-stereoisomer **17** has found indirect support in later efforts by Schiebe[38] in which the oscillator strength of the photogenerated stereoisomer **17** was shown to compare favorably with that of the independently prepared cyclic salt **18** containing the *cis*-C=C configuration.



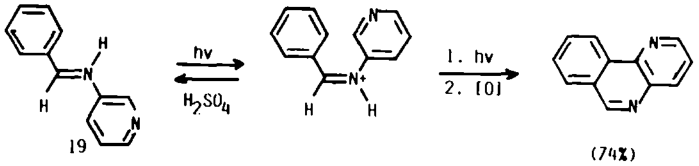
16 17

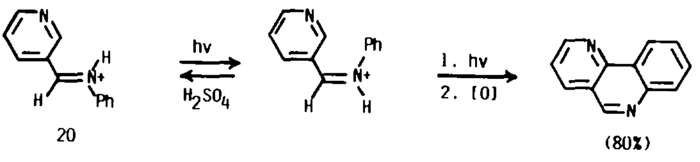


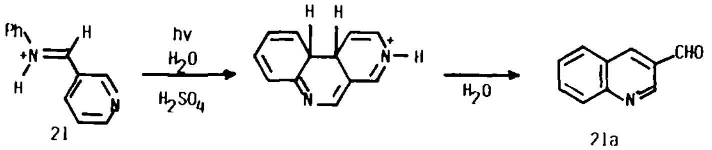
18

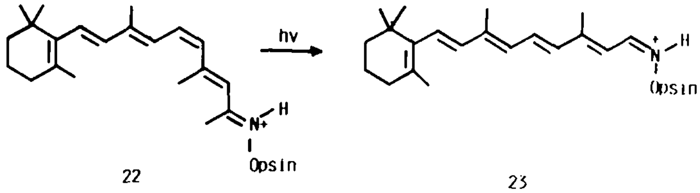
Carbon-nitrogen bond E,Z-isomerization has been detected in only a few photochemical investigations. Perkampus and Behjati[39] invoked rapid E,Z-isomerization processes as initial steps in the stilbene-like photocyclizations of protonated benzylidene amino-pyridines **19** and pyridinalimines **20**. In a similar fashion C=N, E,Z-photoisomerization must be involved in the unusual conversion of the β-pyridinalaniline **21** to quinoline-3-carboxyaldehyde **21a** occurring on irradiation in aqueous sulfuric acid.[40]

A more thorough investigation of C=C and C=N photoisomerizations in α,β-unsaturated iminium salt systems has recently been initiated by Childs and Dickie.[41] Studies in this area are stimulated by thoughts about photochemical events associated with light absorption by the visual pigment, rhodopsin **22**, an iminium salt derived by reaction of 11-*cis*-retinal with a lysine ϵ-amino group of the protein opsin. A key step in the visual process appears to involve photo-initiated

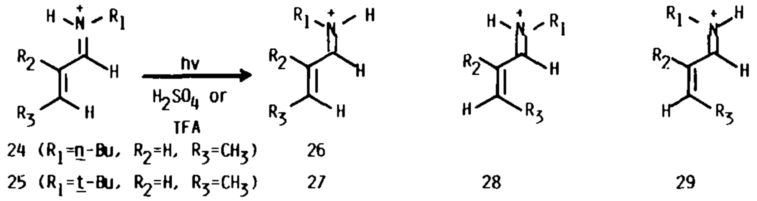




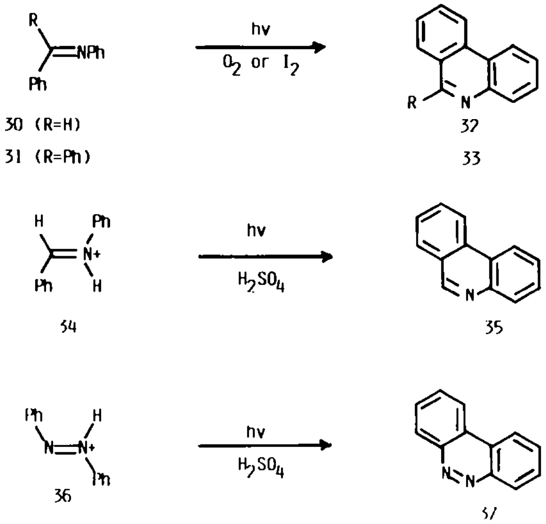




cis–trans isomerization about the $\Delta^{11,12}$ π-bond producing the 11-trans rhodopsin isomer **23**.[42] In order to gain important data about the nature of this process and perhaps related E,Z-isomerizations, Childs and Dickie have conducted detailed studies with a series of iminium salts including **24** and **25**. Efficient C=N isomerization ($\phi(H_2SO_4) = 0.12$, $\phi(TFA) = 0.16$)) is observed when **24** is irradiated in sulfuric acid or trifluoroacetic acid (TFA) generating **26** along with **24** in a photostationary state ratio of 35:65. In contrast, both C=N and C=C isomerization take place in the N-t-butyl systems **25** forming an isomeric mixture consisting of **27**, **28** and **29** along with **25** in a 12:28:10:50 photoequilibrium ratio. The quantum efficiencies for C=C interconversion in the latter case are remarkably solvent dependent ($\phi(H_2SO_4) = 0.17$ and $\phi(TFA) = 0.32$)). Although a detailed analysis of the excited state multiplicity for these transformations is made difficult by the solvent systems employed, the observation that dissolved oxygen has no effect on isomerization efficiencies appears to implicate singlet states as intermediates in these cases.

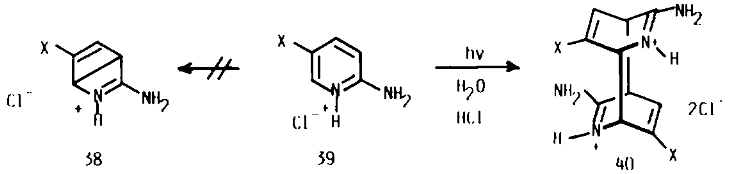


The $\pi - \pi^*$ excited states of iminium salts are expected to participate in other types of photochemical processes which mimic those followed by hydrocarbon analogs. Indeed the photoelectrocyclizations of protonated benzylidenaminopyridines and pyridinalanilines[39,40] discussed above directly parallel the common stilbene to phenanthrene oxidative cyclizations noted in the hydrocarbon series.[43] Another intriguing example of an iminium salt reaction of this type was uncovered by Badger *et al.*[44,45] While the photocyclization of benzalanilines **30** and **31** either do not occur (**30**→**32**) or are exceptionally inefficient (**31**→**33**), the corresponding reactions of their conjugate acids **34**[45] proceed smoothly to produce 9-phenanthridine (**35**) and the diazaphenanthrene **37**.



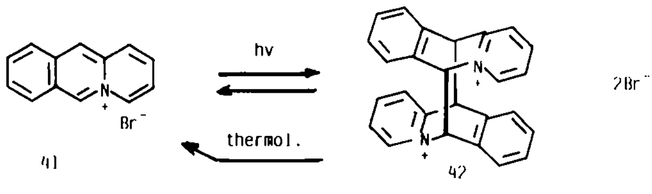
30 (R=H)
31 (R=Ph)
32
33
34
35
36
37

The parallelism between the photochemical behavior of pyridinium and related N-heteroaromatic salts and polynuclear aromatic hydrocarbons is remarkable. Homo and hetero $\pi 4+\pi 4$ cycloadditions of naphthalene and anthracene are well known processes dominating the excited state reactions of these substances. The salts **39** derived by protonation of 2-amino-5-substituted pyridines display similar behavior in their conversion to the 4 + 4-dimers **40** when irradiated in aqueous HCl solutions.[46,47] It should be noted that the earlier communication by Taylor[48] on this subject, erroneously reporting the occurrence of electrocyclization reactions **39**→**38** has been corrected in the later papers. Bradsher *et al.*[49] have uncovered an additional



38
39
40

example of a reaction of this type. Acridizinium bromide (**41**) undergoes $\pi 4+\pi 4$ photodimerization to produce the interestingly layered, tetrabenzotricyclic salt **42** a process directly analogous to the dimerization of anthracene.[50] Bradsher noted that reversion of the dimer **42** to acridizinium salt takes place under thermal activation in ethanol. A more recent investigation of

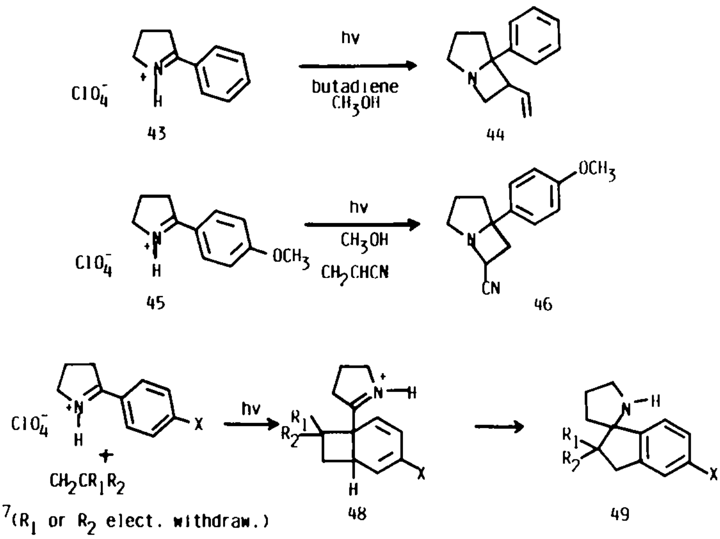


41
42

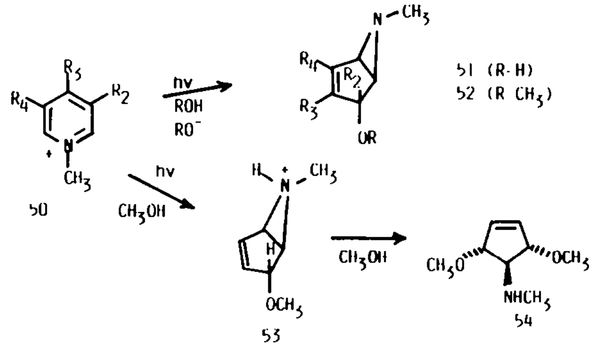
the processes, **41** ⇄ **42** by Kreysig *et al.*[51] has demonstrated that dimer formation is photochemically reversible and that the quantum efficiencies for the forward and retro reactions (0.23 and 0.49 at infinite salt concentration in methanol) are markedly diminished when irradiations are conducted in the presence of neutral or anionic substances which can serve as electron donors (*vide infra*) or enhancers of intersystem crossing. Careful fluorescence spectroscopic analysis of the reacting system led to the conclusion that non-luminescing, singlet excimers serve as intermediates in the dimerization reaction.

It has been known for some time[1,2] that imines are resistant to excited state cycloadditions unless special substitution patterns and ring constraints are present.[52] Photocycloadditions of iminium salts involving addition across the C=N π-bond are likewise rare despite the fact that they would be useful in methods for azetidinium salt synthesis. To our knowledge, the sole observations of olefin-iminium salt photocycloadditions were made in studies of 2-aryl-1-pyrrolinium perchlorate photochemistry. Accordingly, azetidines **44** and **46** are produced when the corresponding pyrrolinium salts **43** and **45** are irradiated in the presence of butadiene[53] and acrylonitrile,[54] respectively. It is interesting to note that the more general reaction of 2-aryl-pyrrolinium perchlorate **47** excited states with electron-poor olefins appears to involve an alternative $\pi 2 + \pi 2$ cycloaddition across the ipso and ortho aromatic ring position leading eventually via **48** to the benzospirocyclic amines **49**.[53,54] The differing courses followed by these reacting systems has been discussed.[54]

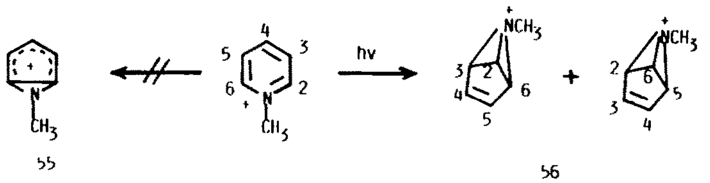
The familiar, photochemically induced, valence bond isomerization reactions of benzene and its derivatives leading to benzvalenes[55] appears to have an analogy in pyridinium salt excited state



chemistry. Thus, irradiations of 1-methylpyridinium chloride and the related picolinium and lutidinium salts **50** in aqueous basic solution, results in production of the 6-azabicyclo(3.1.0)-hex-3-enyl alcohols **51** with reasonably high quantum efficiencies.[56,33] The corresponding methyl ethers **52** are formed upon irradiation in basic methanol. However, when 1-methylpyridinium perchlorate is irradiated in methanol in the absence of base, excellent yields (80%) of the *trans-trans*-dimethoxycyclopentenyl amine **54** are obtained, presumably as a result of secondary solvolysis of the protonated bicycloaziridine **53**.[58] The deuterium and alkyl group



distributions in products formed by irradiation of regiospecifically labelled pyridinium salts has led Wilzbach *et al.* to suggest mechanisms for production of the bicyclic aziridines **51** and **52** which proceed via the azabenzvalene cation **56** followed by nucleophile induced ring opening by attack at either C-6/C-5 or C-3/C-2. An alternative pathway in which the azabicyclohexenyl cation **55** serves as the sole intermediate can be rejected on the basis of the labeling studies since it would not serve to rationalize how carbons 2,3,5 and 6 become equivalent along the reaction pathway.



ELECTRON TRANSFER PHOTOCHEMISTRY OF IMINIUM SALTS

Another important excited state property of substances containing the iminium salt grouping, and one that distinguishes them from hydrocarbon analogs, results from the presence of the positive charge delocalized over nitrogen and carbon. Much of the ground state chemistry of iminium salts including the ability to react with one electron donors is due to this property. The electronic excited states of systems containing the $R_2C{=}\overset{+}{N}R_2$ chromophore should serve as better electron acceptors than the corresponding ground state systems. Indeed, many of the more recently observed photochemical processes followed by iminium salts appear to be nicely rationalized by mechanisms involving initial one electron transfer. Exploratory and mechanistic investigations have uncovered electron transfer pathways in excited state quenching, photosensitization and reaction processes. Spectroscopic detection of radical intermediates generated in these systems has been performed by utilizing a variety of techniques. Moreover, many of the transformations appear to be particularly suited to synthetic practice. In the remaining sections of the report, this area of photochemistry will be discussed, with attention being given to the general features of excited state electron transfer, to evidence supporting mechanistic postulates, and to the general characteristics of electron transfer initiated iminium salt photochemical reaction pathways.

Excited state electron transfer, General concepts

The concepts which serve as the foundation for an understanding of excited state electron transfer have their origins in early investigations of excited state complex formation. The body of data accumulated on this subject suggests that a wide variety of excited state processes occur via the intervention of complexes formed by encounter of excited state molecules with ground state species of the same (forming homodimers or excimers) or different (forming heterodimers or exciplexes) identity.[59] The stabilities of the complexes relative to precursor excited states was initially attributed to exciton resonance interactions involving delocalization of excitation over both components.[60] It is now clear that charge transfer serves as another important component of excited state complex stabilization.[61] This postulate is substantiated by observations which demonstrate that the wavelength maxima for emission from and, thus, energy of exciplexes are dependent upon both the ionization potentials of donors and electron affinities of acceptors in the pairs,[62] and the solvent polarity.[63] In addition, excitation of ground state charge transfer complexes can be used to directly populate the exciplex state.[64] Perhaps the most pertinent information supporting the notion of charge transfer or electron transfer in exciplexes is found in the observed correlations existing between the rate constants for fluorescence quenching and predicted rates of electron transfer in systems for which exchange energy transfer mechanism are inoperative. Weller[65] has noted that relationships exist connecting observed fluorescence quenching rate constants with calculated free energies for electron transfer (ΔG_{et}) in singlet excited donor-acceptor systems. Functions relating electron transfer rate constants (k_{et}) with ΔG_{et} derived by Balzani, Scandola and Schuster[66] on the basis of theoretical considerations have the same general characteristics as those empirically determined by Weller. Accordingly, fluoresence quenching via exciplex formation appears to be controlled by electron transfer, the facility of which is governed by the oxidation and reduction potentials of the donors and acceptors along with the energy of the populated excited state.

An important chemical consequence of charge transfer in excited state complexes is found in the nature of decay pathways available to these systems in polar solvents. Deactivation of singlet exciplexes for example can occur by a number of familiar routes including emission, intersystem crossing, and radiationless decay. However, return to the ground state manifold can take place by a unique pathway involving complete electron transfer with concomitant radical ion formation (eqn 1). Characteristic of this feature is the observation that exciplex lifetimes and emission efficiencies are attenuated in proceeding from solvents of low to high polarity.[67] In addition, exciplex derived, radical ions have been detected by use of various spectroscopic techniques.[68] The charged radical species formed in this way are capable of participating in a number of different chemical processes owing to their high energy content and unique electronic characteristics (*vide infra*).

$$A^* + B \rightarrow \underset{\text{Exciplex}}{\overset{\delta-}{A}\text{---}\overset{\delta+}{B}{}^*} \rightarrow A^{\overline{\cdot}}\,B^{\dot{+}} \tag{1}$$

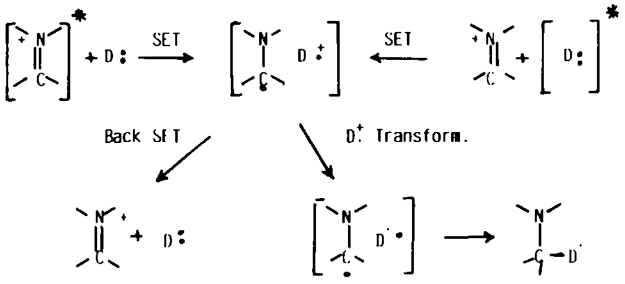
It is possible to develop a qualitative framework for predicting when electron transfer pathways will compete with alternate modes of excited state decay. A simplified molecular orbital view of redox systems serves to demonstrate the axiom that electronic excited states are both better one electron donors and acceptors than the corresponding ground state species. Thus, the excitation energy of the system ($\Delta E_{0,0}$) serves as the thermodynamic driving force for electron transfer. A more precise formulation of the relationship between ΔG_{et} and oxidation ($E_{1/2}(+)$) and reduction ($E_{1/2}(-)$) potentials and $\Delta E_{0,0}$ is presented in eqn (2).[65b] Furthermore, the empirically derived relationship between ΔG_{et} and k_{et} suggests that the rate constants for electron transfer will approach the diffusion controlled limit (*ca* $1 \times 10^{10}\ M^{-1}\ sec^{-1}$) when electron transfer is exoergic ($\Delta G_{et} < 0$). Therefore, preliminary information on the possible operation of electron transfer mechanisms in a particular photochemical process can be gained by considering the experimentally determined ground state electrochemical potentials and excited state energy of the donor acceptor pair and solvent polarity, and by comparing the calculated value for k_{et} with rate constants for other excited state deactivation modes.

$$\Delta G_{et} = E_{1/2}(+) - E_{1/2}(-) - \Delta E_{0,0} - C \tag{2}$$

Another important consideration in developing a framework for understanding excited state processes initiated by electron transfer is the nature of the species which serve as reactive intermediates. The chemical selectivities of classical photochemical processes are often influenced by properties of the excited state intermediates including electron density distributions, orbital symmetries, and their unique nuclear coordinant versus energy distribution functions. Thus, reaction barriers which prohibit certain reaction types in the ground state manifold are in some cases easily surmounted by excited state systems.[69] Photosensitization by exchange energy transfer in which excitation energy is conveyed with conservation of multiplicity from sensitizer to acceptor serves as another mode for activating excited state reaction pathways. The facility of this indirect method for forming potentially reactive excited states is governed by the relative excited state energies of sensitizers and acceptors. The factors controlling excited state reactions proceeding by electron transfer mechanisms are distinctly different from those at work in classical photochemical processes. For example, in electron transfer sensitized processes the energetics of electron transfer determine the rates and efficiencies for sensitizer activation of acceptor molecules. Many examples exist in which electron transfer photosensitization occurs even though classical energy transfer is extremely endoergic.[70] More importantly, the character of excited state electron transfer initiated processes will reflect that fact that neutral or ion radicals serve as the key reactive intermediates. Thus, a framework for describing and predicting the chemical behavior of these processes can be developed by considering the reaction modes available to species of this type. Pertinent information can be found by inspecting electron impact or capture mass spectrometric fragmentations[71] and solution phase electrochemical transformations.[72] It is perhaps not surprising to find that the fundamentals summarized above have been frequently used in recent years to rationalize and design a number of novel and interesting excited state reactions.

Electron transfer pathways in iminium salt photochemistry

Calculations which take into account excited state energies and ground state reduction potentials of various iminium salts and related heteroaromatic cations suggest that systems containing the $R_2C{=}\overset{+}{N}R_2$ grouping should serve as ideal acceptors in electron transfer initiated photochemical processes. Typical donors should include olefins and arenes (π-type) and alcohols and ethers (n-type) Approximate free energies for electron transfer from ground state donors in each of these classes to singlet excited states of typical iminium and N-heteroaromatic salts are included in Table 2. Iminium salts can also participate in photochemical processes by serving as ground state acceptors of electrons from excited states of donor systems (Table 3). Both modes of electron transfer lead to production of α-amino radicals as part of radical pair (intermolecular et) or diradical (intramolecular et) intermediates in pathways for excited state quenching or reaction as outlined in Scheme 3.



Scheme 3.

Before detailing some of the characteristics of iminium salt excited state reactions proceeding by electron transfer mechanisms, it will be instructive to reivew the results of studies in which spectroscopic methods have been employed to gain information about the nature of electron transfer in these systems. The large electron affinity of salts of N-heteroaromatic systems is reflected

Table 2. Free energies for electron transfer from selected ground state donors to singlet excited states of iminium and N-heteroaromatic salts

Iminium and N-Heteroaromatic Salts				$\Delta G_{et}{}^{d}$ (kcal/mol) from Electron Donors			
Compound	$E_{1/2}{}^{S_0}(-)^{a}$ (Volts)	$\Delta^{S_1}E_{0,0}{}^{b}$ (eV)	$E_{1/2}{}^{S_1}(-)^{c}$ (Volts)	$(CH_3)_3COH$	THF	$(CH_3)_2C{=}CH_2$	$PhCH_3$
1-Methylpyridinium ClO_4	-1.3	4.3	+3.0	-11.5	-25.3	-16.1	-39.1
1-Methylquinolinium ClO_4	-0.9	3.5	+2.6	-0.2	-16.1	-6.9	-29.9
2-Methylisoquinolinium ClO_4	-1.0	3.5	+2.5	0.0	-13.8	-4.6	-27.6
2-Phenyl-1-pyrrolinium ClO_4	-1.0	3.9	+2.9	-9.2	-23.0	-13.8	-36.8

a) Value for pyridinium salt from ref. 72, for quinolinium and isoquinolinium salts from ref. 15 and for pyrrolinium salt from ref. 73.

b) See Table 1 for sources of these data.

c) Singlet excited state reduction potentials calculated according to $\Delta E^{S_1}(-) = \Delta E_{0,0} + E_{1/2}{}^{S_0}(-)$.

d) Calculated by method of Weller (ref. 65b) by using the following values for donor oxidation potentials, $(CH_3)_3COH$ (+2.5V), THF (+1.9V), $(CH_3)_2C{=}CH_2$ (+2.3V) and $PhCH_3$ (+1.3V) and ignoring solvent effects.

Table 3. Free energies for electron transfer from singlet excited state donors to ground states of iminium and N-heteroaromatic salts

Iminium and N-Heteroaromatic Salts		ΔG_{et}[c] (kcal/mol) Singlet Donors[d]			
Compound	$E_{1/2}^{S_0}$ (-)	$PhCH_3$	Naphthalene	Anthracene	t-Stilbene
1,2-Dimethyl-1-pyrrolinium ClO_4^-	-2.0[a]	-13.6	+13.6	+2.5	-13.8
1-(2-Propylidene)pyrrolidinium ClO_4^-	-1.95[a]	-14.8	+1.48	+1.3	-1.50
$(CH_3)_2C{=}\overset{+}{N}(CH_3)Ph\ ClO_4^-$	-1.63[a]	-22.1	-22.1	-6.0	-22.3
$Ph(CH_3)C{=}\overset{+}{N}(CH_3)_2\ ClO_4^-$	-1.49[a]	-25.3	-25.3	-9.2	-25.5
1-Methylpyridinium ClO_4^-	-1.3[b]	-27.2	-27.2	-11.5	-27.3
1-Methylquinolinium ClO_4^-	-0.85[b]	-40.2	-40.2	-21.9	-40.3
2-Methylisoquinolinium ClO_4^-	-1.00[b]	-36.6	-36.6	-18.4	-36.8

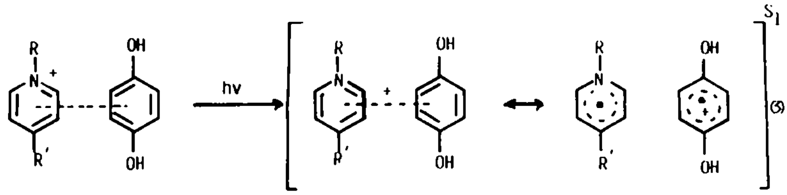
a) Data taken from ref. 21.

b) Data taken from ref. 72.

c) Calculated by using the Weller equation (ref. 65b) and ignoring solvent effects.

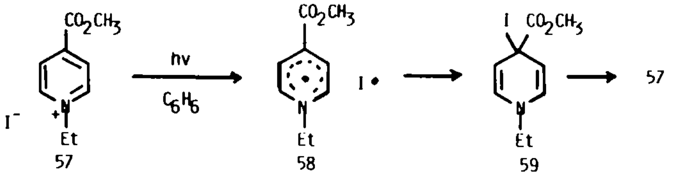
d) Singlet excited state oxidation potentials, calculated from $E_{1/2}^{S_1}(+) = E_{1/2}(+) - \Delta E_{0,0}$ are $PhCH_3$ (-2.6V), naphthalene (-2.5V), anthracene (-1.8V), and t-stilbene (-2.6V).

in their propensity to form ground state charge transfer complexes with a variety of anionic and electron rich aromatic donors. In independent studies, LaGoff,[74] Nasielski,[75] and Kosower[76] have characterized charge transfer complex formation between pyridinium and quinolinium salts and pyrene, the cyclopentadienylide anion and the iodide ion. Perhaps the best known of these systems is 1-ethyl-4-carbomethoxypyridinium iodide where transition energies (Z values) derived from the CT-band UV-maxima are used as a measure of solvent polarity.[77] The herbicide, paraquat dichloride, forms strong charge transfer complexes with a series of aromatic hydrocarbons including pyrene, naphthalene, stilbene and phenol which absorb at longer wavelengths in the UV-visible spectrum than either of the donor or acceptor components.[78] In a few cases, such as with phenolic donors, the paraquat CT-complexes can be isolated as crystalline substances.[79] It is interesting that the λ_{max} for the p-hydroquinone paraquat dichloride complex experiences a shift to shorter wavelengths in proceeding from solvents of lower (CH_3OH, λ_{max} 450 nm) to higher (H_2O, λ_{max} 400 nm) polarity or dielectric constant. This change in transition energies as a function of solvent polarity suggests that charge separation is greater in the ground versus singlet excited state of this complex. This is not necessarily expected for cases in which the CT-complexes are comprised of neutral donors and charged acceptors. However, the result appears to be in accord with both a reduction or change in the dipole of the complex upon excitation resulting from a greater degree of electron transfer from donor to acceptor (eqn 3) and a slow reorganization of solvent dipoles compared to the rate of electronic transition.



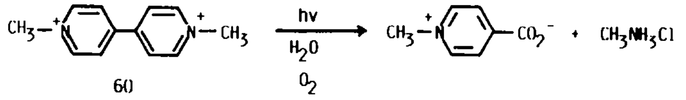
(5)

Detailed information about the nature and degree of electron transfer in excited states of CT-complexes derived from N-heteroaromatic salts has come from flash photolysis investigations of the 1-ethyl-4-carbomethoxypyridinium iodide system by Kosower.[80] The short lived 1-alkylpyridinyl radical pair, produced by irradiation of the corresponding pyridinium iodide **57** in benzene, can be detected by uv techniques (λ_{max} 395 nm). Decay of **58** appears to proceed via a complex pathway involving the intermediacy of the 4-iodo-1,4-dihydropyridine **59**. A more thorough analysis of the fate of iodine atoms produced by irradiation of 1-methyl-pyridinium, -collidinium and -quinolinium iodides has been performed by Cozzens and Gover.[81] The transient absorbing below 300 nm and above 650 nm upon flash photolysis of these iodides is attributed to $I_2^{\cdot -}$ based upon comparisons with spectra of independently prepared iodine radical anion. Additional evidence has been provided to support the mechanisms for production of $I_2^{\cdot -}$ shown in eqn (4).

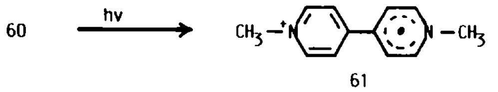


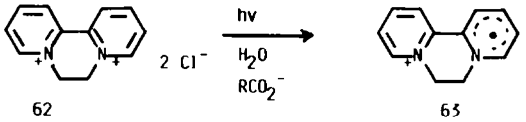
$$\text{Py}^{+}\text{I}^{-} \xrightarrow{h\nu} \text{Pyr}^{\cdot}\text{I}^{\cdot} \xrightarrow{\text{I}^{0}} \text{Pyr}^{\cdot}\text{I}_2^{\cdot -} \tag{4}$$

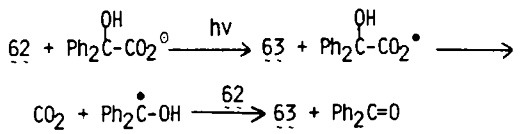
Paraquat **60** and related dications have been the targets of numerous studies exploring excited state electron transfer due to their use as herbicides and the unusual photodegradiation reactions occurring under environmental conditions (eqn 5).[82] As is the case with other N-heteroaromatic salts, irradiation of paraquat dichloride in aqueous buffered-solutions leads to generation of the paraquat radical cation **61**.[83] The lifetime of this transient intermediate ranges from 200 μs at pH 0 to one-week at pH 12. It is likely, therefore, that the photooxidative degradation of paraquat outlined in eqn (5) is initiated by electron transfer followed by addition of molecular oxygen to **61** and subsequent dihydropyridine ring cleavage. Ledwith *et al.*[84] have found that analogous excited state processes occur when paraquat or diquat dichloride **62** are irradiated in solutions containing formate, oxalate or benzilate anions. Cation radical **63** formation induced by irradiation of the diquat acid salt CT complex occurs from the single state of diquat since fluorescence quenching rate constants are near the diffusion controlled limit (1×10^{10} M^{-1} sec^{-1}) in water. Lastly, electron transfer in the diquat-benzilate anion system is associated with production of benzophenone by the route outlined in Scheme 4. Similar processes have been observed in the ferric ion-induced conversion of benzilic acid to benzophenone.[85]



(5)





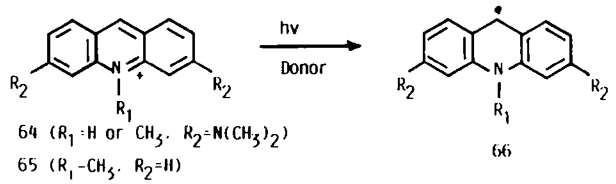


$$62 + Ph_2\overset{OH}{C}-CO_2^{\ominus} \xrightarrow{h\nu} 63 + Ph_2\overset{OH}{C}-CO_2^{\bullet} \longrightarrow$$

$$CO_2 + Ph_2\overset{\bullet}{C}-OH \xrightarrow{62} 63 + Ph_2C{=}O$$

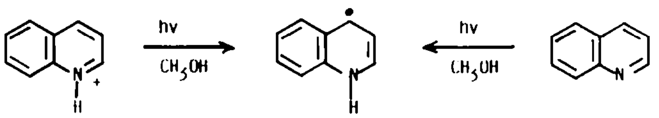
Scheme 4.

Numerous additional studies have provided results which demonstrate the generality of electron transfer in the excited state chemistry of N-heteroaromatic salts. Correlations of quenching rate constants with donor oxidation potentials for example, have been used to invoke electron transfer mechanisms for formation of the acridine orange radicals **66** from the triplet states of the cation precursors **64**.[86] Similarly, the fluorescence of the N-methylacridinium cation **65** is quenched by a range of counterions with efficiencies which depend directly upon the quencher reduction potentials and inversely upon solvent polarity.[87] Finally, bromide and iodide ion quenching of acridizinium salt **41** fluorescence and $\pi 4 + \pi 4$ dimerization (*vide supra*) are fully consistent with electron transfer in the singlet excited manifold.[51]

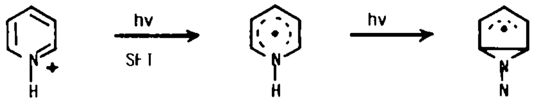


64 ($R_1 = H$ or CH_3, $R_2 = N(CH_3)_2$)
65 ($R_1 = CH_3$, $R_2 = H$)
66

One of the more thorough studies of excited state electron transfer in N-heteroaromatic salts has been conducted by Lablache-Combier through the use of ESR-spectroscopic techniques. The N-protonated salts of pyridine, quinoline, 4-methylquinoline, isoquinoline and 9-phenylacridine (e.g. **67**) were shown to undergo photoconversion to their characterizable semiquinone radicals (**68**) when irradiated in acidified methanol or ether. Interestingly, the same semiquinone radicals (**68**) are generated by irradiation of the parent heterocycles in methanol by mechanisms involving hydrogen atom abstraction from methanol by the $n - \pi^*$ excited state systems. In a related ESR study, Lablache-Combier[89] has provided evidence for formation of the 2-azabicyclo [3.1.0] hexenyl radical (**69**) upon irradiation of pyridine hydrochloride in a glass (H_2O) matrix. A two photon pathway, involving initial electron transfer followed by a 5-π-electron disrotatory photoelectrocyclization appears to be operable in this case.



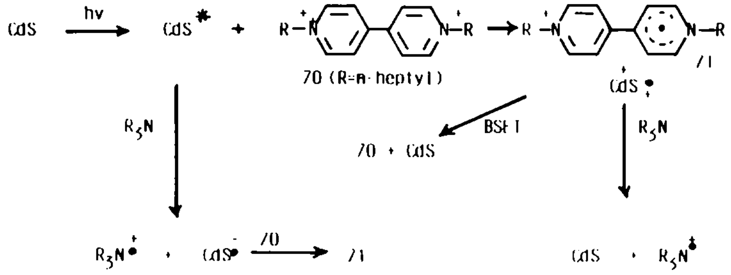
67 68



69

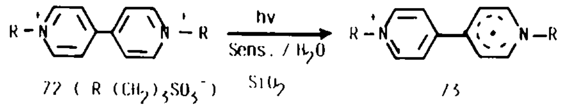
The involvement of iminium salts in electron transfer photochemistry can be in ways other than as excited state electron acceptors. Several recent observations show that systems containing this grouping can serve as ground state electron acceptors in reactions with electronically excited donors or with radical intermediate produced in a primary photochemical event. For example, irradiation of non-aqueous solutions of heptylviologen **70** containing suspended cadmium sulfide with light of wavelengths sufficient to selectively excite the semiconductor results in production of the cation radical **71**.[90] The rate of production of non-semiconductor bound **71** as measured by ESR spectroscopy was enhanced *ca* 250-fold by the addition of tertiary amines such as triethanolamine.

These intriguing results appear to be consistent with mechanisms in which irradiation of the semiconductor with light of energy greater than the band gap creates a hole in the valence band and a singly occupied conduction band. Thus, the electronically excited CdS can serve as both a single electron oxidizing and reducing species. Accordingly **71** can be produced by electron transfer from excited CdS to the dication **70** or from the cadmium sulfide radical anion itself produced by electron transfer from the tertiary amine to the valence band hole of the excited semiconductor (Scheme 5). An alternate mode of tertiary amine catalysis of heptylviologen radical cation formation might involve trapping of $CdS^{\dot{+}}$ in competition with rapid back electron transfer which destroys **71** (Scheme 5).



Scheme 5.

Another example in which a N-heteroaromatic salt serves as an electron acceptor in reaction with an excited state electron donor is found in the zinc meso-tetramethylpyridinium porphorin and Ru $(bpy)_3{}^{2+}$ photosensitized generation of propyl viologensulfonate anion radical **73** occurring upon irradiation in solutions containing colloidal SiO_2 and triethanolamine.[91a] Here, as in the case above, electron transfer from sensitizer to the dication **72** occurs at the solid-liquid interface to produce **73**. The tertiary amine serves as a catalyst for reconversion of sensitizer from oxidized back to reduced forms. Analogous pathways are operable in the sensitized photoreduction of methylviologen by the dye, proflavin.[91b]

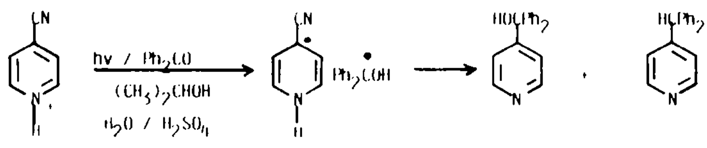


Salts of N-heteroaromatic compounds can participate in yet another type of photostimulated electron transfer process in which radicals produced in primary photochemical events serve as electron donors. An intriguing example of this indirect electron transfer route has been uncovered in studies by Hyde and Ledwith[92a] of paraquat salt photoreductions induced by irradiation of typical aryl ketone triplet sensitizers in aqueous-isopropylalcohol solutions. Accordingly, irradiation ($\lambda > 366$ nm) of benzophenone or xanthone solutions containing isopropylalcohol and the dication **60** results in production of the radical cation **61**. The accumulated data from an extensive study of this system are best explained in terms of electron transfer to **60** from the ketyl radicals **74** and **75** produced by triplet ketone hydrogen atom abstraction from isopropyl alcohol (Scheme 6).

$$Ph_2C{=}O \xrightarrow[\substack{2\ \text{ISC} \\ 3.\ (CH_3)_2CHOH}]{1\ h\nu} \underset{\textbf{74}}{Ph_2\dot{C}{-}OH}\ \ \underset{\textbf{75}}{(CH_3)_2\dot{C}{-}OH} \xrightarrow{\textbf{60}} Ph_2C{=}O + (CH_3)C{=}O + \textbf{61}$$

Scheme 6.

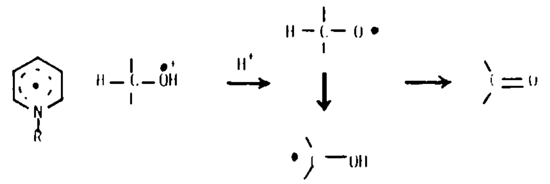
A reaction pathway mimicking that proposed by Ledwith appears to be operating in the photoinitiated substitution reactions of protonated 4-cyanopyridine **76** occurring by irradiation of benzophenone in aqueous isopropyl alcohol and 1M H_2SO_4 solutions.[92b]

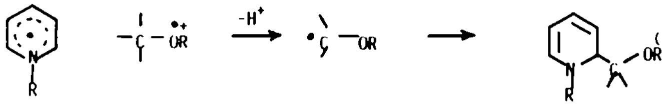


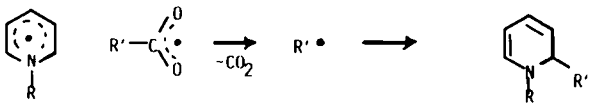
76

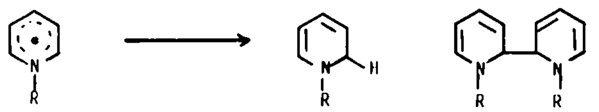
PHOTOCHEMISTRY OF N-HETEROAROMATIC SALTS

Pyridinium and related N-heteroaromatic cationic systems participate in a wide variety of electron transfer induced excited state processes the more characteristic of which involve photooxidations, photoreductions and photoadditions. An excellent review describing a number of these transformations has been written.[93] In general, the type of the reaction pathways followed in these systems depends upon the nature and fate of the donor derived neutral (if a negatively charged donor is used) or cation (neutral donor) radical and the hydropyridinyl and related radicals produced in the electron transfer step. As will be seen, electron transfer from, alcohols bearing α-hydrogens to excited, N-heteroaromatic salts can be part of alcohol oxidation (eqn 6) and alcohol or ether addition (eqn 7) processes. Carboxyl radicals generated by electron transfer from carboxylate anions can undergo decarboxylation in pathways leading to alkylation of the N-heteroaromatic system (eqn 8). Lastly, 1-hydropyridinyl and related radicals can serve as precursors to either reduction or dimeric products depending upon the reaction conditions employed (eqn 9). The mechanistic details and synthetic potential of these processes will be discussed in the remaining parts of this section.


(6)


(7)

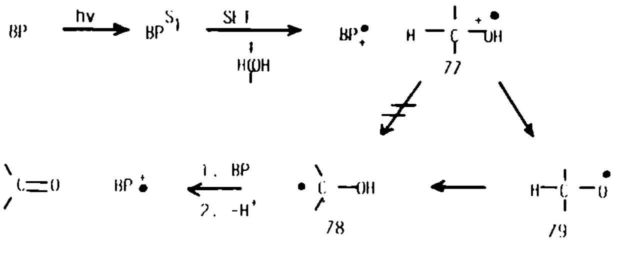

(8)


(9)

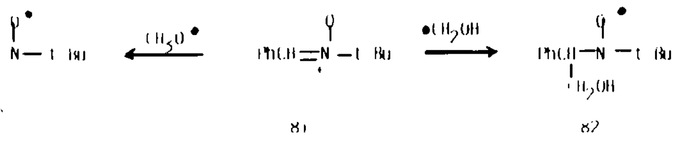
Electron transfer induced alcohol oxidations

The redox chemistry of alcohol N-heteroaromatic cation systems has been thoroughly investigated principally by Ledwith and his co-workers by use of a variety of bipyridylium cations.[94] The large reduction potentials of paraquat dichloride ($E_{1/2}(-) = -0.45$v) and diquat dihalides ($E_{1/2}(-) = -0.35$v) serve as the driving force for electron transfer in the ground and excited state manifolds. It is well known, for example, that the corresponding radical cations are formed upon exposure of these salts to aqueous alkali solutions or to methoxide ion in methanol.[95] Similarly, UV irradiation of diquat or paraquat dichloride in aqueous solutions containing primary or secondary alcohols produces the blue cation radicals.[96,97] In both cases, oxidation of the alcohols occur to yield carbonyl products in near quantitative yields. Cation radical formation and alcohol oxidation appear to be singlet state processes based upon the observed correspondence between efficiencies for reaction and fluorescence quenching by halide ions, phenol and ferrocene. Additional information on the mechanistic details of these processes comes from isotope effect results. The deuterium isotope effects for both alcohol oxidation and quenching of diquat fluorescence are in the range of *ca* 1.4 for both OD and α-CD substitution, suggesting that electron rather than hydrogen atom transfer is involved in the rate determining step common to both processes.

Electron transfer from alcohols to the singlet states of the bipyridylium salts **BP** would yield the **BP** cation radical and the alcohol derived cation radical **77** which can undergo deprotonation from oxygen or the α-carbon generating the respective alkoxy or hydroxyl alkyl radicals, **79** and **78** (Scheme 7). Ledwith has provided indisputable evidence in the form of spin trapping results that the alkoxy radical is formed initially under these conditions.[98,99] Accordingly, the nitroxyl radical **80** is detected by ESR of solutions produced by irradiation of paraquat in the presence of methanol and the nitrone **81**, a common radical spin trap.[100] Interestingly, the nitroxyl radical **82**, formed by capture of the hydroxymethyl radical is detected when the concentration of spin trap **81** is low. Likewise spin trapping experiments employing a nitroso butane demonstrated that products of hydroxymethyl radical capture were produced. These results indicate that the rate of conversion of the initially formed alkoxy radicals to the more stable hydroxyalkyl radicals is rapid under the photoreaction conditions. Independent measurements show that the rate constants for these transformation are *ca* 1 × 10^7 sec^{-1}, thus confirming the spin trapping results.[101,102] The final step in the oxidation sequence appears to involve electron donation by the hydroxyalkyl radical to the bipyridylium salt in the ground state. Evidence is available implicating a second pathway of this type for $BP^{\dot{+}}$ formation.[97,102]



Scheme 7.

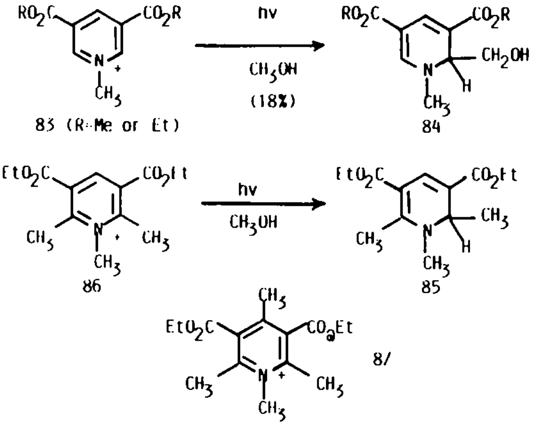


A detailed kinetic analysis of these photoredox reactions has been recently published.[104,105] One of the intriguing observations in this series of studies concerns the fact that t-butyl alcohol efficiently quenches diquat chloride fluorescence, presumably by an electron transfer mechanism, yet heteroaromatic cation radicals are not formed in detectable quantities when the bipyridylium salts are irradiated in aqueous t-butyl alcohol.[97] A necessary consequence of these observations is that the radical cations are formed but that they undergo rapid and efficient oxidation concurrent with reduction of t-butoxy radical to the corresponding alkoxide. This has been substantiated by the observation that t-butoxy radicals generated by photolysis of di-t-butyl peroxide or thermolysis of di-t-butyl hyponitrite are quantitatively transformed to t-butoxide in the presence of paraquat radical cation.[106]

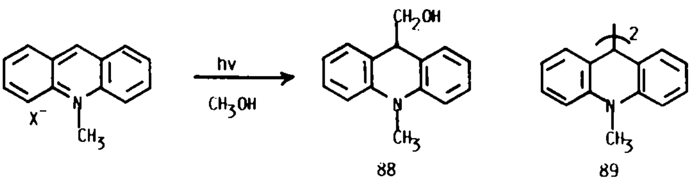
Photoaddition of alcohols and ethers to N-heteroaromatic salts

In the alcohol oxidation reactions described above, electron transfer to the excited states of bipyridylium salts initiate hydroxyalkyl and N-heteroaromatic cation radical pair formation. The fate of the intermediate hydroxyalkyl radicals and, thus, the nature of the overall reaction appears to be governed by the great stability of the bipyridylium cation radicals and high efficiency for oxidation of hydroxyalkyl radicals by the ground state dicationic systems. Simple, mono-cationic N-heteroaromatic salts do not possess these properties and, as a result, alternate pathways such as coupling serve as effective reaction modes. Substituted pyridinium and related mono-and diazaaromatic salts fall into this category. In these cases, carbon–carbon bond formation can occur between the hydroxyalkyl and 1-hydropyridinyl and related radicals at positions of high odd electron density in the delocalized systems.[24]

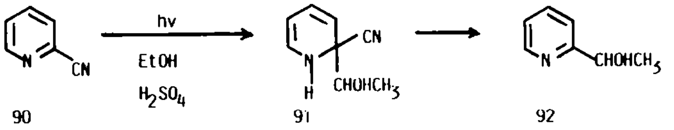
A variety of reactions between N-heteroaromatic salts and alcohols or ethers appear to fit this pattern. An early example is present in photochemical studies by Van Bergen and Kellogg[107a]



of pyridinium carboxylic esters **83**, **85** and **87**. Irradiation of **83** in methanol results in production of the bright yellow 1,2-dihydropyridinylmethanol **84**. The corresponding methylsubstituted salts **85** and **87** do not display similar behavior but rather generate reduction products, as in the case of **85**, or are unreactive (e.g. **87**). Likewise, N-methyl-acridinium salts undergo photohydroxymethylation upon irradiation in methanol to yield the 9-hydroxymethylacridanes **88** along with the 9,9′-*bis*-acridanes **89**.[84] Other interesting examples of reactions of this type are found in

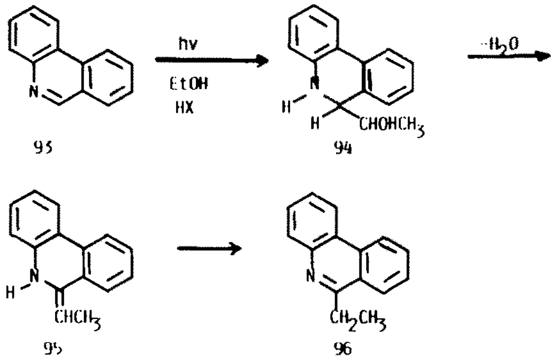


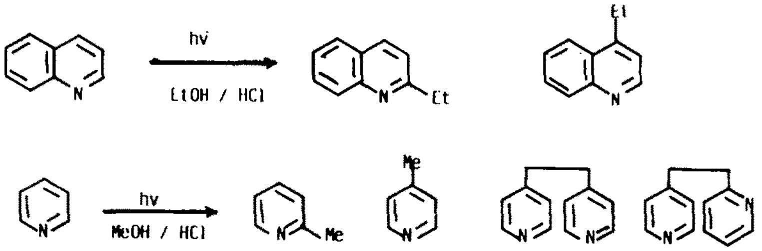
the excited state chemistry of N-protonated 2-cyanopyridine **90**.[107b] Thus, formation of the 2-pyridylethanol **92** by irradiation of ethanol solutions of **90** containing sulfuric acid can be rationalized by electron-transfer induced addition providing the dihydropyridine **91** followed by elimination of hydrogen cyanide.



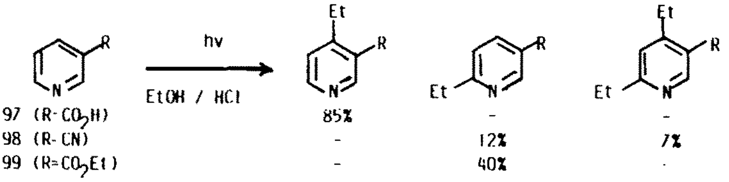
In a number of cases, alcohol adducts derived by photoaddition to N-heteroaromatic salts are unstable under the acidic reaction conditions and undergo dehydration to yield products formally coresponding to alkylation pathways. One of the earliest examples of this reaction type was uncovered by Stermitz *et al.*[107c] in photochemical studies with phenanthridine (**93**). Irradiation of

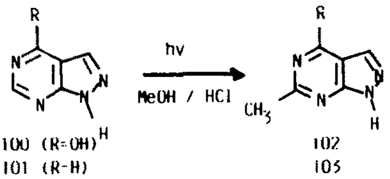
93 in acidified ethanol solution was shown to furnish 10-ethylphenanthridine (**96**) in essentially a quantitative yield via a route involving initial formation of the ethanol adduct **94** followed by dehydration to **95** and tautomerization. A wide variety of simple N-heteroaromatic compounds including quinoline and pyridine participate in analogous alkylation reactions.[107c,108,111] The substituent dependence of photoalkylation regiochemistry is reflected in the photochemistry of nicotinic acid **97** and its derivatives **98** and **99**.[112] The preferences observed for formation of either the 4- or 6-ethyl-pyridines appear to be controlled by a combination of 3-substituted-1-hydropyridinyl radical odd electron densities (slightly greater at C-4 than C-6)[24] and steric factors (favoring C-6).



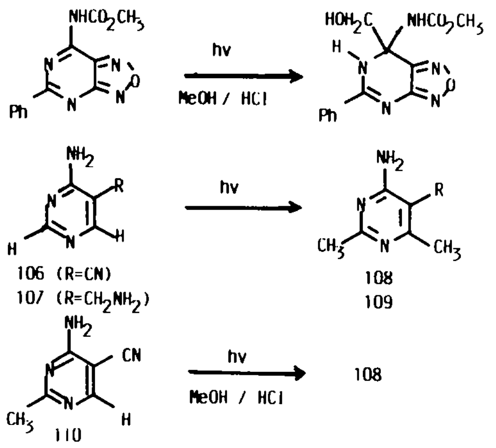


N-heteroaromatic substances containing purine and pyrimidine ring systems also undergo photoalkylation by electron transfer mechanisms when irradiated in acidic solutions of primary alcohols. One example is present in studies of allopurinol (**100**), a potent inhibitor of xanthine oxidase used in the treatment of gout. Ochiai and Morita[113] found that the 2-methyl derivative **102** is efficiently produced (67%) by irradiation of **100** in 2% HCl in methanol. The related 4-amino



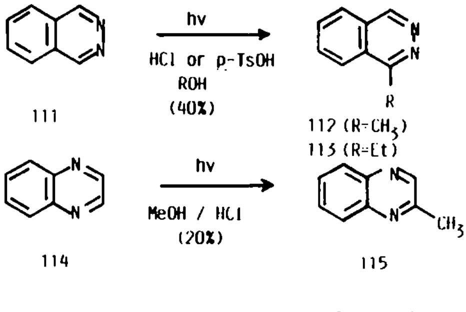


purine **101** undergoes methylation at the 2-position under these conditions to form **103** (47%). Interestingly, electron-transfer induced methanol addition to the oxadiazole ring containing pyrimidine **104** occurs regioselectively at C-4 giving the stable adduct **105**.[114] Other substituted pyrimidines **106**, **107** and **110** are transformed to mono- and di-methylated adducts by irradiation in acidic methanol through mechanistic pathways related to those outlined above.[113] Evidence supporting the proposed mechanism for these reactions is present in results by Ochiai and Morita[115]

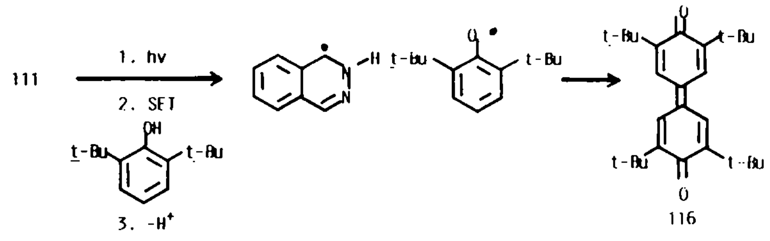


which demonstrate that substantial quantities of the hydroxymethyl radical are produced by irradiation of acidic methanol solutions containing pyrimidine bearing electron withdrawing groups at C-5 and that the alkylation reaction efficiencies are uneffected by changes in acid type and concentration.

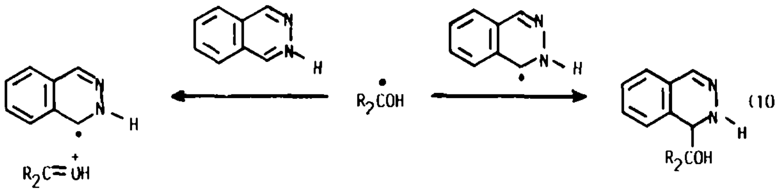
A detailed study of phthalazine **111** and quinoxaline **114** photochemistry by Wake and his co-workers[116] has uncovered interesting photoalkylation reactions as examplified by the transformations **111**→**112** and **113**, and **114**→**115**. It is important to note that these heterocyclic substances do not undergo photoalkylations when irradiated in acidic isopropanol. The lack of reactivity in these cases appears to be associated with the ready oxidation of the intermediate hydroxyisopropyl radical by ground states of protonated phthalazine and quinoxaline. Detailed information supporting this notion is lacking, however. Irradiation of phthalazine in trifluoroacetic



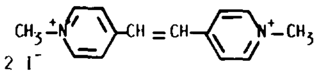
acid solution containing 2,6-di-*t*-butylphenol leads to formation of the *bis*-dienone **116** and recovered heterocycle. In this case, the phenoxy radical formed from the phenol by sequential electron-proton transfer must undergo dimerization leading to **116** rather than coupling with the intermediate hydrophthalazinyl radical.



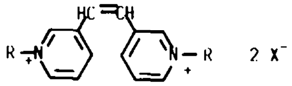
A comparison of the quantum yields for photoalkylation of phthalazine ($\phi(CH_3OH) = 0.026$, $\phi(EtOH) = 0.0055$, $\phi((CH_3)_2CHOH) = 0$) points out another interesting feature of these photoalkylation reactions. Accordingly, photoaddition quantum yields are inversely related to alcohol oxidation potential. Thus, the rate of initial electron transfer from alcohol to the excited state of the phthalazinium cation must not be governing the overall reaction efficiencies. Rather, partitioning of the intermediate hydroxyalkyl radicals by coupling to hydrophthalazinylradical *versus* electron transfer to ground state phthalazinium cation (eqn 10) seems to control alkylation efficiencies. Indeed, the hydroxyalkyl radical oxidation potentials should parallel those of the corresponding alcohols ($HO\dot{C}H_2 > HO\dot{C}HCH_3 > HO\dot{C}(CH_3)_2$) and influence electron transfer rates.



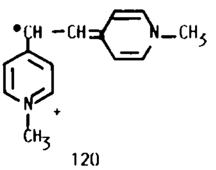
Analogous, electron transfer induced, photoaddition reactions occur when the dipyridylethylene dications **117–119** are irradiated in the presence of THF and diethyl ether.[117,118] Here, sequential electron–proton transfers give rise to radical pairs (e.g. **120**) which couple at the ethylene carbon centers of highest odd electron density to produce adducts **121** and **122**. Additional studies have shown that the 4,4′-bipyridylethylene dication undergoes efficient electron transfer induced *cis-trans*-isomerization upon irradiation in the presence of a variety of one-electron donors such as ethers and tertiary amines.[119]



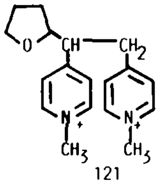
117



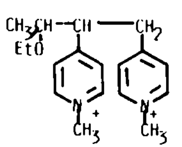
118 (R=CH$_3$)
119 (R=H)



120

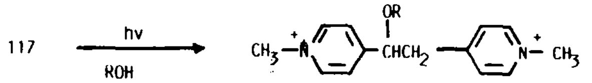


121



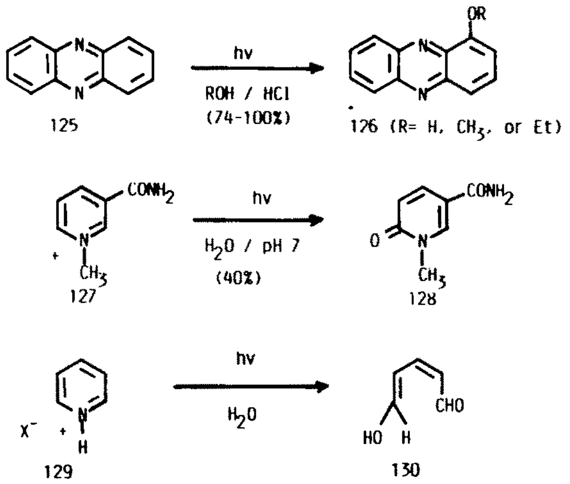
122

An intriguing change in photochemical reactivity is observed when excited states of these dications interact with nucleophiles such as water or ethanol. Products of nucleophilic addition to the ethylene moieties (e.g. **123** and **124**) are produced with high chemical and quantum yields. A rationalization for both the nature and regiochemistries of these photoreactions has been provided by Whitten[117] in terms of the results of MO calculations which suggest that a large decrease in electron density occurs at the ethylene carbons upon singlet excitation of the dipyridylethylene dications. Related photoinduced, nucleophilic additions analogous to those described by Whitten,



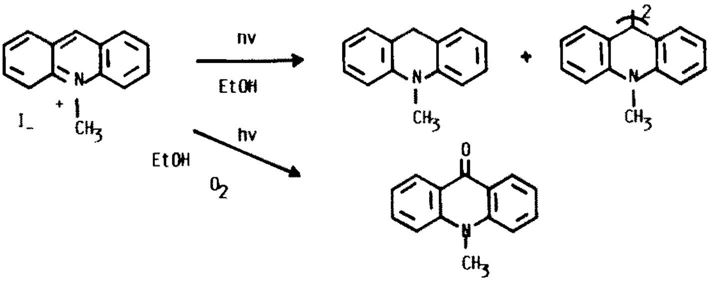
123 (R=H)
124 (R=Et)

but where attack takes place on the N-heteroaromatic cation ring system, are common in a number of pyridinium and related salt systems. Processes of this type are known to compete with radical substitutions in 2-cyanopyridinium salt photochemistry,[106] to dominate the excited state reaction profiles of phenazinium dications (**125**→**126**)[120,121] despite the operation of competitive but nonproductive electron transfer,[122] and to be responsible for the photoconversion of pyridinium salts to α-pyridones (**127**→**128**)[127] and glutaconic aldehyde (**129**→**130**).[124]



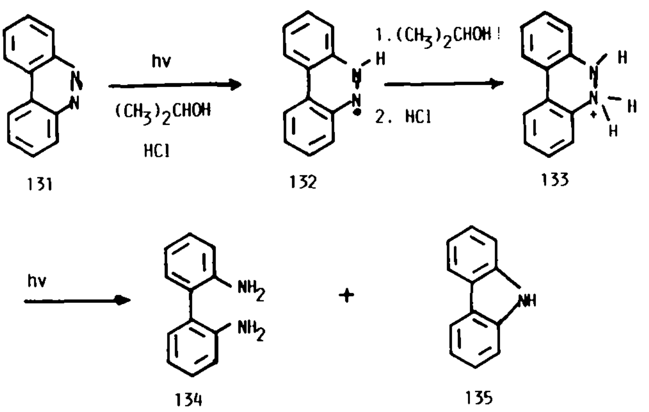
Photoreductions and photodimerizations of N-heteroaromatic salts

The hydropyridinyl and related radicals generated by excited state electron transfer from alcohols and other donors undergo other typical free radical reactions such as hydrogen atom abstraction and coupling as part of processes leading to photoreduction and photodimerization of the N-heteroaromatic salts. One example demonstrating both reaction types has been provided by Zanker *et al.*[125,126] in study of N-methylacridinium iodide photochemistry. Irradiation of this salt in ethanol under anaerobic conditions leads to efficient generation of 9,10-dihydroacridine and the 9,9′-dimer. When oxygen is included in the photolysis medium, trapping of the acridinyl radical occurs and 10-methyl-9-acridone is ultimately produced. The actual species, iodide anion or ethanol, serving as the electron donor in the initial step of these pathways is still undetermined.

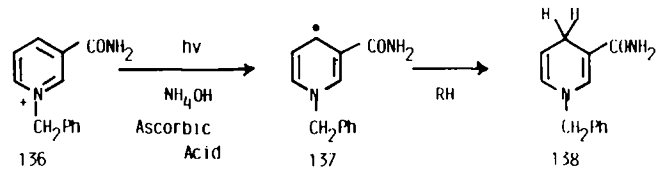


Electron spin resonance techniques have been employed to detect and identify radical cation intermediates in the photoconversions of phthalazine and cinnoline (**131**).[127] Intermediates of this type (e.g. **123**) must be responsible for excited state reduction occurring upon irradiation of **131** in acidic isopropyl alcohol solution and producing the unstable, protonated hydrazine **133**. Detailed investigations by Inoue[128,129] have provided data supporting assignment of the triplet state of **131** as the reactive species and hydrazine **133** as the precursor for the isolated photoproducts, diamine **134** and carbazole **135**.

Studies of the reduction reactions of pyridinium salts containing electron withdrawing groups at the 3-position have been numerous, presumably owing to their potential relationship to the biologically important redox transformations of the NAD–NADH coenzyme system. A variety of chemical and electrochemical methods have been employed in converting N-substituted nicotinamide salts to 1,2-,[130] 1,4-,[131,132] and 1,6-dihydro[133] products. In addition a number of early

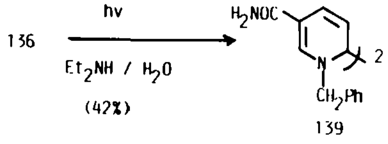


reports suggested that irradiation of NAD or its analogs in the presence of ascorbic acid gives reduced nicotinamides, detected by UV-spectroscopic analysis.[134-137] More recent efforts by Matsurra[138] have confirmed these results by showing that the 1,4-dihydronicotinamide **138** can be isolated from the photolysate derived by irradiation of **136** in ammonium hydroxide solution containing ascorbic acid. Other hydrogen atom donating, reducing agents such as catechol can be

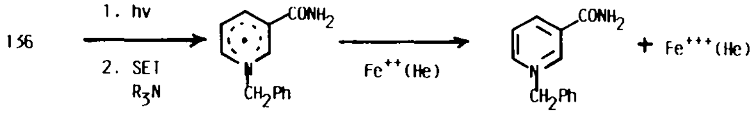


used to affect reduction, but replacement of ammonium hydroxide in the reacting system by tertiary amines or potassium hydroxide fails to induce product formation.

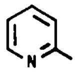
Different behavior is observed when the pyridinium salt **136** is irradiated in aqueous diethyl amine or EDTA solutions. Kano and Matsuo[139,140] proposed that the 6,6′-nicotinamide dimer **139** is generated under these conditions by a route involving excitation of the amine-**136** charge transfer complex followed by electron transfer. Kano[141] demonstrated in continuing investigations of this system that the hydropyridinyl radical **137** serving as an intermediate for dimerization and other, related radicals can be used to drive Hemin ($Fe^{2+}He$) reduction. Accordingly, formation of reduced

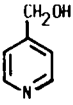


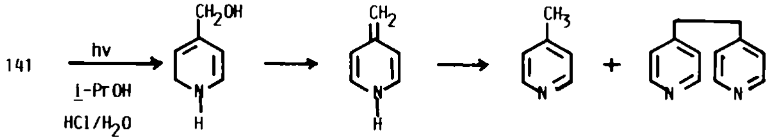
Hemin containing the Fe^{3+} ion, as detected by increases in absorption at the characteristic wavelength maxima 526 and 556 nm, occurs when a mixture of $Fe^{2+}He$ and **136** are irradiated in the presence of EDTA or TMEDA (eqn 11).



Several additional examples emphasize the mechanistic intricacies of pyridinium salt electron transfer photochemistry. Stenberg[142] has shown that the photoconversions of 2- and 4-pyridinyl carbinols, **140** and **141**, to the corresponding picolines and dipyridylethanes (e.g. **143** and **144**) by irradiation in aqueous acidic isopropyl alcohol solutions involve initial electron transfer induced reduction to dihydropyridines (e.g. **142**). Acid catalyzed dehydration followed by tautomerization or dimerization would then complete the sequences. Photoreduction of pyridinium salts can also be stimulated by electron transfer from excited state of electron rich donors. This reverse electron transfer route has been invoked by Ogata[143] to explain the conversion of diester **145** to the 1,6-dihydro product **146** which occurs upon visible light irradiation of zinc tetraphenylporphyrin (ZnTPP) in aqueous micellar solutions of sodium laurylbenzenesulfonate and ascorbic acid. Production of **146** by an electron transfer mechanism is consistent with observations that **145** quenches the fluorescence of ZnTPP even though classical energy transfer would be highly endoergic and that N-methylnicotinamide resists reduction under these conditions owing to its low reduction potential.


140

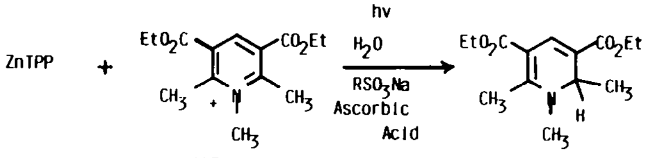

141



142

143

144

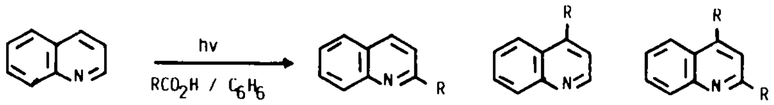


145

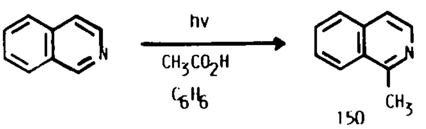
146

Electron transfer induced photoalkylations between N-heteroaromatic compounds and carboxylic acids

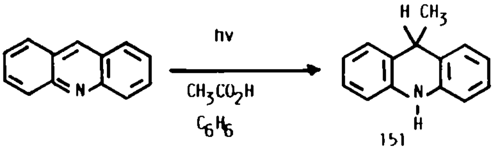
Thus far, we have seen that pyridinium and related salts containing the iminium cation grouping participate as acceptors in excited state electron transfer processes and that the resulting 1-hydropyridinyl and related radicals undergo various radical reactions including hydrogen atom abstraction, dimerization and addition to radicals derived from the electron donors. Excited state decarboxylative additions of carboxylic acids to N-heteroaromatic compounds appear to fall in the latter category. in these cases, electron transfer from carboxylate to N-heteroaromatic ions provides carboxyl radicals which readily lose CO_2, to produce alkyl radical precursors of addition products. Formation of the alkyl-substituted quinolines **147**, **148** and **149** by irradiation of the parent heterocycle in benzene solutions of acetic, propionic or isobutyric acid followed by oxidative work up serve as examples of this pathway.[144] Isoquinoline and acridine participate in similar alkylation reactions yielding the 1-methyl and 10-methyl adducts, **150** and **151**. The potential synthetic utility of these reactions is demonstrated by the reasonably efficient formation of 2-*t*-butylquinoline **152** from quinoline and pivalic acid,[144] and by the employment of intramolecular versions for



R	147	148	149
Me	40%	20%	5%
Et	40%	-	10%
i-Pr	35%	27%	9%

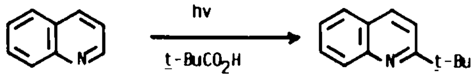


150

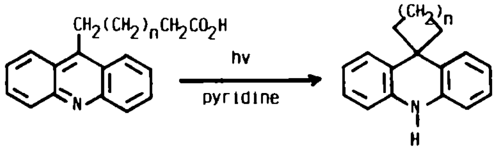


151

carbocyclic ring formation as in the cases of the acridinylbutyric and valeric acids **153**.[145] It is interesting to note that the substituted phenanthridines **154** ($R=CH_3$, Ph or $PhCH_2$) display different behavior when irradiated in the presence of dichloroacetic, acetic or propionic acid. In these cases

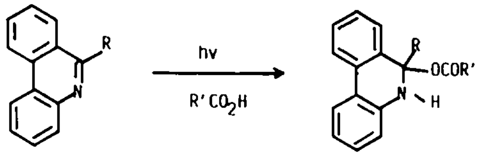


152



153

products such as **155** corresponding to nucleophilic addition rather that decarboxylative alkylation are formed exclusively.[146]

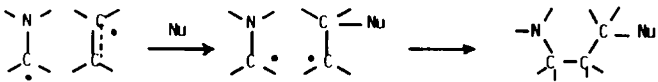


154 155

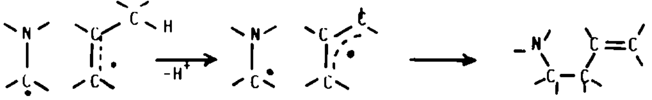
ELECTRON TRANSFER PHOTOCHEMISTRY OF NON-AROMATIC IMINIUM SALTS

General overview

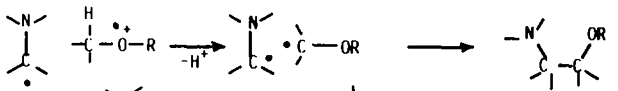
As discussed earlier in this report, simple iminium salts possess electronic properties which make them ideally suited for participation in electron transfer initiated, excited state processes. Recent studies have demonstrated that this is indeed the case. Accordingly, excited states of conjugated iminium salts serve as efficient acceptors in one electron transfer processes with a variety of neutral donors including electron rich olefins, arenes, alcohols and ethers. Furthermore, the reaction pathways followed by these systems are governed by the nature and chemical behavior of initially formed, donor derived cation radicals. Photoaddition and photocyclization reactions outlined schematically in eqn 12–15 can be attributed to the facility of nucleophilic addition, de-



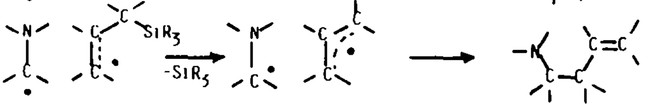
(12)



(13)



(14)



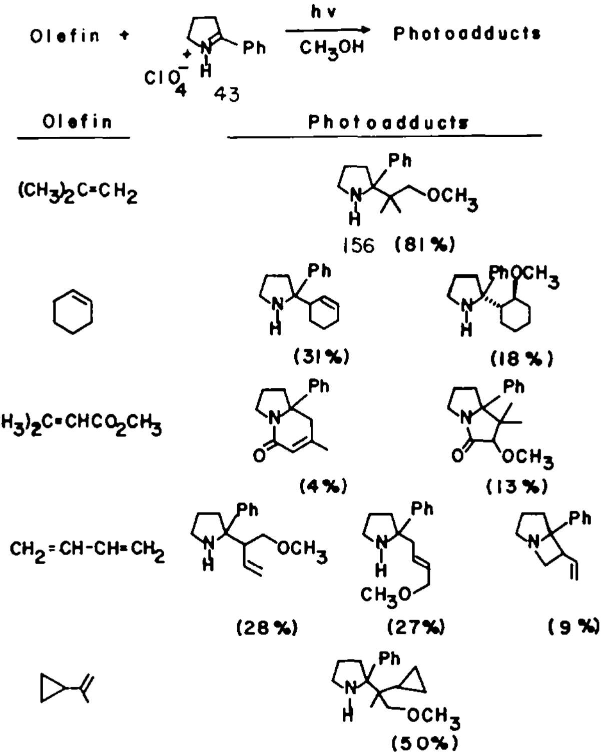
(15)

protonation and desilylation of cation radical intermediates. Furthermore, cation radical pair precursors to addition products can arise via electron transfer from excited states of electron rich donors to iminium salt ground state systems. In the remaining sections of this report, the mechanistic and synthetic consequences of photoreactions initiated in these ways will be summarized.

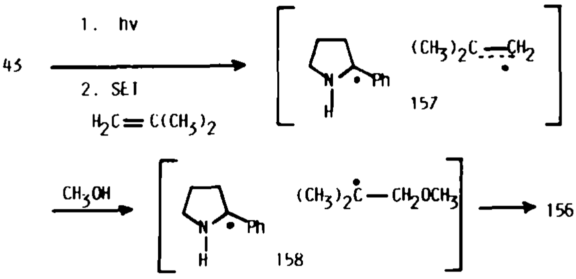
Olefin-iminium salt photoaddition reactions

Novel photoaddition reactions of the type outlined in eqn 12 have been uncovered in initial studies designed to assess the efficiency and chemical consequences of electron transfer from π-type donors to excited states of systems containing the iminium cation chromophore. The free energies and rates of electron transfer to singlet excited states of C-phenyl conjugated iminium salts are predicted to be favorable when olefins with $E_{1/2}(+) < ca$ 2.6 V are employed as donors. The observation that several electron rich olefins serve as excellent quenchers of 2-phenyl-1-pyrrolinium perchlorate (**43**) fluorescence is consistent with this expectation.[147] Rate constants for quenching in these cases are near the diffusion controlled limit (*ca* $1 \times 10^{10}\,M^{-1}\,s^{-1}$) eventhough classical quenching by the exchange energy transfer pathway is prohibited due to extreme endoergicity (*ca* +10 to +20 kcal/mol).

The photochemical reaction pathways followed by simple olefin minimum salt systems are reflective of electron transfer activation. For example, irradiation of **43** in methanolic solution containing isobutylene ($E_{1/2}(+) = ca$ +2.3 V) leads to efficient production of the methoxyalkylpyrrolidine **156**. Similar reactions occur between **43** and a number of other electron rich olefins including cyclohexene ($E_{1/2}(+) = ca$ +2.0 V), butadiene ($E_{1/2}(+) = ca$ 2.2 V), methyl $\beta\beta$-dimethylacrylate ($E_{1/2}(+) = ca$ +2.7 V), and isopropenylcyclopropane.[53,147] The structural

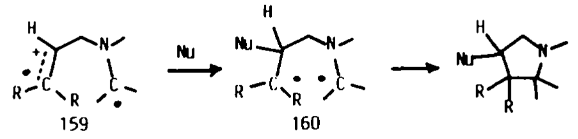


outcome and regiochemical selectivities of these photoaddition reactions can be rationalized by electron transfer mechanisms, outlined in Scheme 8 for the case of isobutylene, in which methanol attack on the olefin derived, cation radical intermediate **157** occurs at the least substituted carbon to form the ultimate radical pair **158**. This is followed by carbon–carbon bond formation. A qualitative test was employed to substantiate this postulate. Electron transfer from the electron poor olefins acrylonitrile, methyl methacrylate having $E_{1/2}(+) > +3.0$ V to $\mathbf{43}^{S_1}$ should be inefficient. This is reflected in their small rate constants for quenching of **43** fluorescence. Significantly, β-aminoether adducts like those formed in reactions of electron rich olefins are not generated upon irradiation of **43** in methanolic solutions of these electron poor olefins. Instead, epimeric spirocyclic amines are generated by pathways involving $\pi 2 + \pi 2$ arene-olefin cycloaddition and ring expansion.[54,147,148]



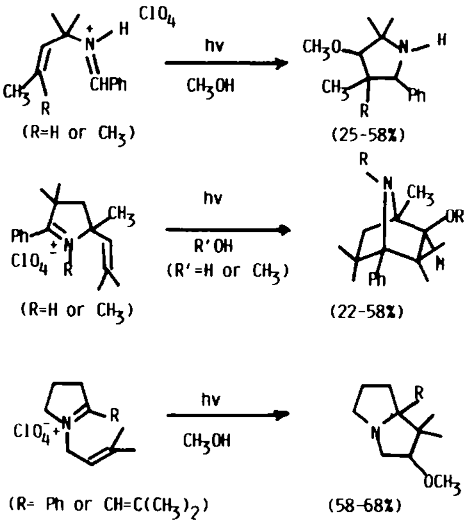
Scheme 8.

Intramolecular counterparts of the photoaddition reactions of the type described in eqn 12 have been used to construct interesting heterocyclic ring systems. Results from our investigations of various N-allyliminium salt systems show that electron transfer initiated photocyclizations occur to generate 3-pyrrolidinyl ethers or alcohols in monocyclic, and bridged or fused bicyclic environments. Several early examples of transformations which demonstrate this feature are accumulated in Scheme 9.[148,149] In these cases, the cyclization regiochemistry is controlled by selective generation of 2-aza-1,5-diradicals **160** through nucleophilic addition to the less substituted positions of the cation diradicals **159** arising by intramolecualr electron transfer. Examples which

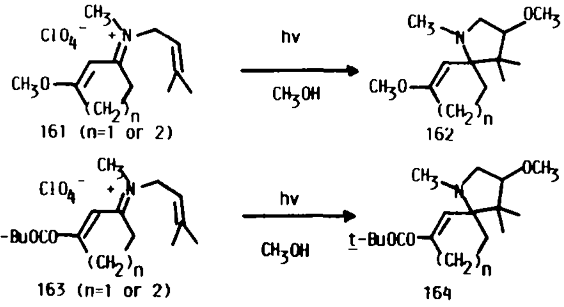


further demonstrate the structural versatility of these photocyclization reactions are found in the transformations of the β-enaminone derived salts **161** and **163** to the corresponding spirocyclic amines **162** and **164**.[150]

An evaluation of excited and ground state electrochemical potentials along with considerations of a number of spectroscopic and chemical observations allows the prediction that electron rich olefins should serve as efficient donors in electron transfer induced addition and cyclization reactions with appropriately substituted N-heteroaromatic salts. This postulate has been tested through the use of spectroscopic methods and by exploratory studies of photochemical behavior.[14] The fluorescence of the quinolinium and isoquinolinium perchlorate **165–168** is efficiently quenched ($k_q \sim k_{diff}$) by various electron rich olefins, including tetramethylethylene, α-pinene and cyclohexene, even though operation of classical energy transfer mechanisms is prohibited. In addition, electron withdrawing substituted olefins like acrylonitrile serve as less efficient quenchers for these salts as would be expected for quenching by an electron transfer mechanism. A further indication of this feature comes from inspection of the fluorescence quantum yields for N-methyl, N-allyl and N-prenylquinolinium (**166**, **169**, **170**) and -isoquinolinium (**168**, **171**, **172**) perchlorates. In both series, replacement of the N-methyl group by the olefin containing allyl and prenyl sidechains results in dramatic decreases in ϕ_f. The diminution of ϕ_f by nearly two orders of



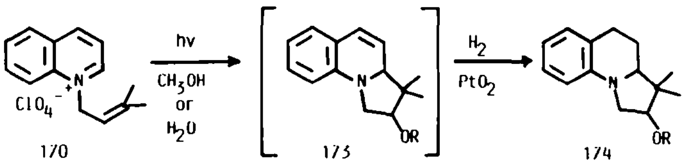
Scheme 9.

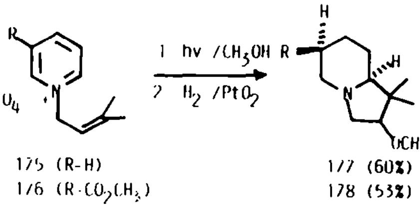


magnitude in both cases appears to be due to decreases in singlet lifetimes brought about by reversible, intramolecular electron transfer. Chemical aspects of electron transfer have been tested in exploratory studies with N-prenylquinolinium and pyridinium perchlorates **170**, **175** and **176**.[14] Irradiation of aqueous or methanolic solutions of **170**, followed by reduction of the intermediate

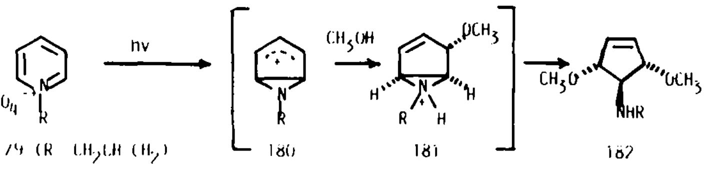
165	(R=H)	167
166	(R=CH$_3$)	168
169	(R= CH$_2$-CH=CH$_2$)	171
170	(R= CH$_2$-CH=C(CH$_3$)$_2$)	172

dihydroisoquinoline **173**, leads to formation of the benzoindolizidines **174**. The yields of these processes (21–27%) are low due to competitive photofragmentation which generates quinoline and products of solvent capture of the prenyl cation. The pyridinium perchlorates **175** and **176** undergo analogous photocyclizations to yield the indolizidine ethers **177** and **178** when subjected to the irradiation-hydrogenation sequence.



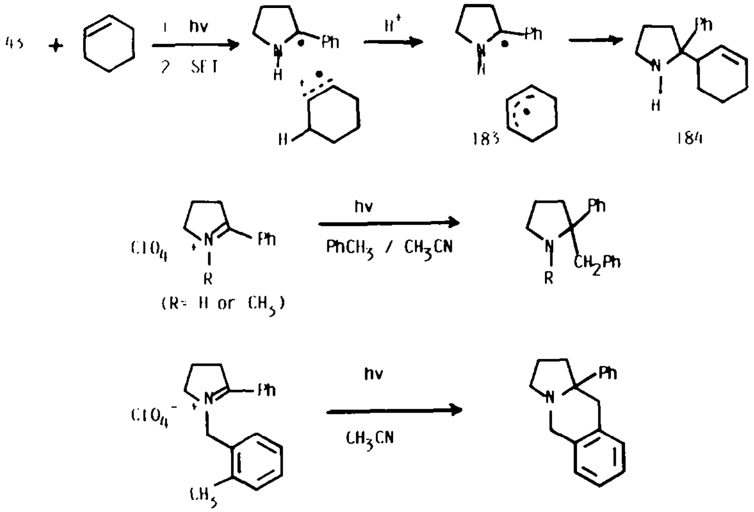


Additional information about the nature of these heteroaromatic salt photocyclizations has come from studies with the simple N-allylpyridinium perchlorates **179**. The efficiency of intramolecular electron transfer from olefinic to excited charged heterocyclic moiety in these salts should depend upon the degree of alkyl substitution on the alkene grouping owing to the relationship between charge stabilization and oxidation potential. A manifestation of this is found in the photochemistry of **179**. Irradiation of **179** in methanol leads to formation of the aminocyclopentene **182** in a remarkably high chemical yield (86%).[14] A mechanism similar to that proposed by Wilsbach[56] to rationalize the photochemical transformation of N-methylpyridinium chloride under strongly basic conditions to a bicycloamino alcohol appears to be responsible for this process. Accordingly, capture of the bicyclic allyl cation **180** formed by electrocyclization of **179** gives the protonated azabicyclohexene **181**, an intermediate which upon methanolysis forms **182**, It is clear from a comparison of the quantum yields for reaction of **175** and **179** (ϕ = 0.04 vs 0.0024) that cyclopentene formation would poorly compete with electron transfer induced cyclization in cases where the allyl side chain is highly alkyl substituted.



Sequential electron–proton transfer and related reactions

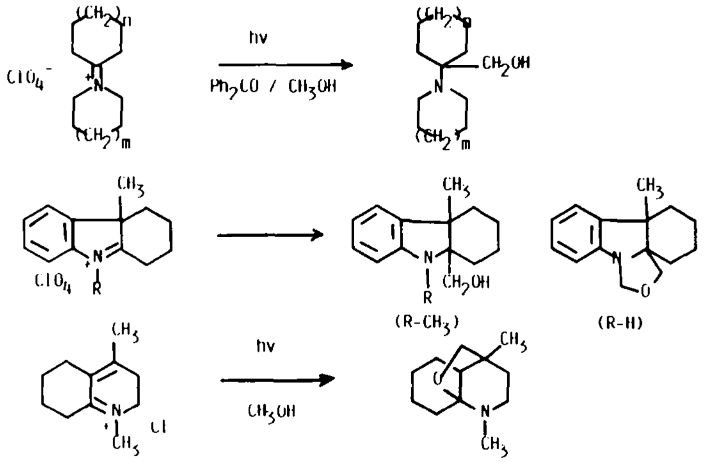
Observations made in studies of the cyclohexene-pyrrolinium perchlorate **43** photoaddition reactions outlined above indicate that another reaction pathway might be available to cation radicals generated by excited state electron transfer. Specifically, formation of the cyclohexenylpyrrolidines **184** most probably occurs via the radical pair **183** generated by sequential electron–proton transfers. Analogous mechanisms must be operating in the inter- and intramolecular photobenzylations exemplified by the reactions included in Scheme 10.[151] More generally, reactions of this type fit into a broader group of electron transfer initiated processes, activated by



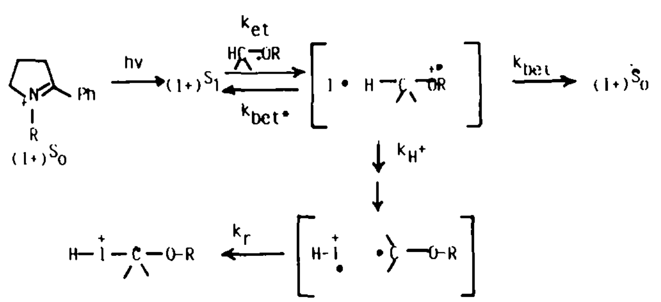
Scheme 10.

loss of electrofugal groups from sites β to the cation radical centers. Indeed, a variety of photoreactions of this type have been uncovered in studies of amine-olefin additions,[152] β-aryl ether cleavages, 153 and α-amino acid[154] and 2-arylacetic acid [155] decarboxylations.

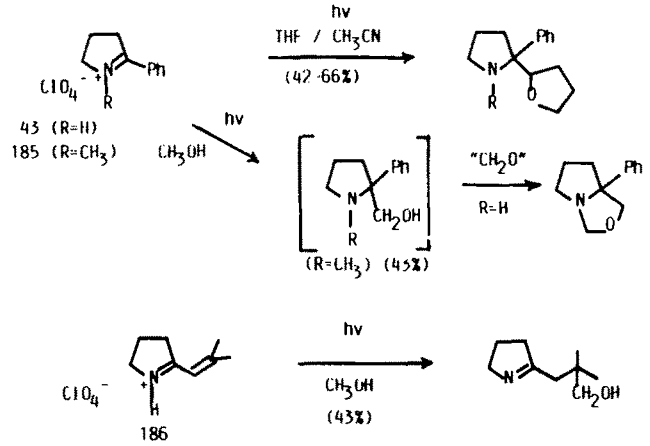
Alcohol and ether photoadditions to iminium salts comprise another family of reactions activated by sequential electron-proton transfer. Our efforts in this area were preceded by several studies which had uncovered a number of interesting examples of methanol photoadditions to simple iminium salts, included in Scheme 11.[156] More detailed photophysical and photochemical studies with the pyrrolinium perchlorates **43** and **185** have provided a mechanistic framework to more fully understand these processes.[157] The OD and CD deuterium isotope effects on the rate constants for **43** and **185** fluorescence quenching by alcohols and ethers along with the correlations of k_q with estimated oxidation potentials of the quenchers are indicative of pathways for iminium salt, singlet state deactivation involving electron transfer. The mechanism for fluorescence quenching shown in Scheme 12 accounts for these data. Furthermore, inclusion of proton transfer as one of the steps in the fluorescence quenching pathway is justified by the expectation that electron transfer in these systems would be endoergic (i.e. $k_{bet^\bullet} > k_{et}$) or only slightly exoergic and by the observation that t-butyl alcohol, with the lowest oxidation potential but lacking α-hydrogens serves as a poor quencher. The photoaddition reactions involving the perchlorate salts **43**, **185** and **186** summarized in Scheme 13 are consistent with these mechanistic postulates. Furthermore studies with the tertiary alcohol, 1,2,3-trimethylcyclopropan-1-ol, provides additional useful information about the natures of the fluorescence quenching and reaction processes. The comparative rate constants for pyrrolinium salt fluorescence quenching by this tertiary alcohol and t-butyl alcohol demonstrate that the former is a much better quencher. Thus, the cyclopropane ring in this cyclopropanol must in some way be involved in the mechanism for quenching. It has been proposed[157] that the facility of C–C bond cleavage in the radical cation **187** introduces a new



Scheme 11.

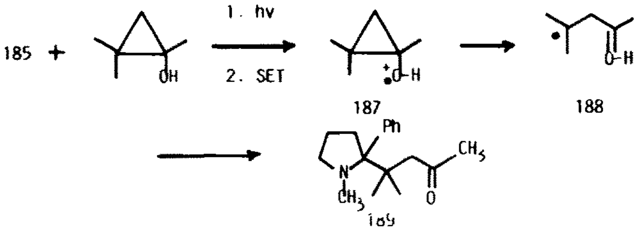


Scheme 12.



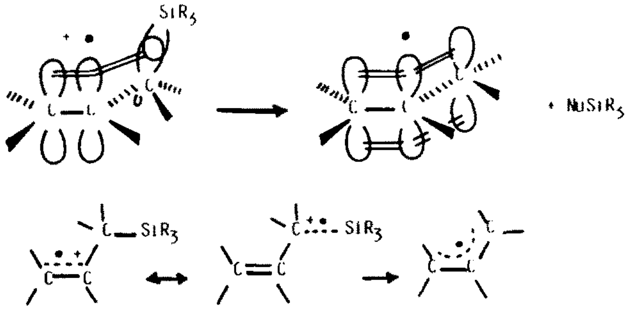
Scheme 13.

reaction mode (**187**→**188**) which would compete with back electron transfer producing the pyrrolinium salt singlet excited state. An alternative view, based upon observations made in studies of the electron transfer photochemistry of strained ring compounds,[158] is that conjugation of the hydroxyl and cyclopropane groups in the cyclopropanol leads to a lower oxidation potential and, thus, enhanced electron donating properties. Consistent with either rationale is the observation that this alcohol undergoes photoaddition to **185** to produce the pyrrolidinyl ketone **189**. Thus, ring cleavage of the intermediate cation radical **187** is yet another example of a general mode for activating electron transfer reactions.



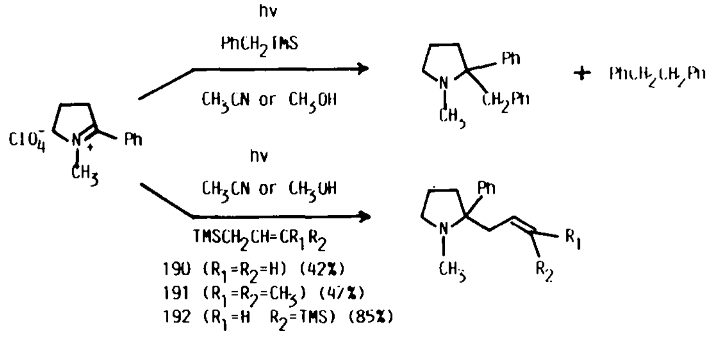
Allylsilane photoadditions to iminium salts

The results of our studies with olefin, arene, alcohol and ether-iminium salt systems suggested that cation radicals, generated by electron transfer from n- or π-type electron donors, undergo elimination of protons β to the charged site to form radical precursors of addition and cyclization products. These transformations serve to exemplify the general electron-electrofugal group transfer route outlined above. The reasoning embodied in this scheme has been used in designing additional systems to test mechanistic postulates and to probe the synthetic potential of this class of excited state reactions. For example, it expected that cation radicals generated from allyl or benzyl silanes would undergo rapid desilylation in the presence of even weak nucleophiles (Scheme 14) owing to



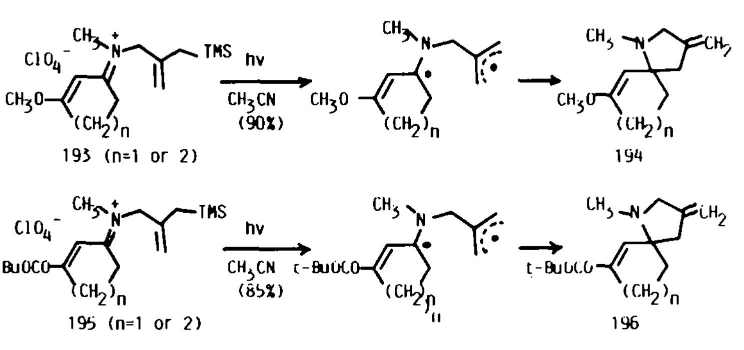
Scheme 14.

favorable σ (C–Si bond)-π interactions and the weak and polarized C–Si bond.[159] This electron transfer desilylation sequence would constitute an efficient method for generation of allylic or benzylic radicals capable of serving as precursors to addition products. Indeed, the efficient photoaddition reactions observed to occur between the pyrrolinium perchlorates **43** and **185** and benzyltrimethylsilane[151] and the allyl silanes[159] (Scheme 15) demonstrate the validity of this postulate. Evidence to support the conclusion that mechanisms for these reactions involve nucleophile induced desilylation prior to carbon–carbon bond formation is found in the regiochemical selectivities for additions of the allylsilanes **191** and **192**. In both of these, the direction of addition appears to be controlled by steric factors which guide C–C bond formation in the ultimate radical pair to the less substituted, allylic radical carbons. Alternative pathways in which attack of the allylsilane occurs on the high energy singlet excited iminium cation or where cation radical pair coupling precedes desilylation would produce the unobserved, regioisomeric adducts.



Scheme 15

The synthetic potential of allylsilane-iminium salt photochemistry has recently been tested in studies directed at the development of novel spirocyclization methodologies.[150] Accordingly, the iminium salts **193** and **195**, prepared by 0-alkylation or 0-acylation of the corresponding β-enaminoketones, were found to undergo efficient cyclization upon irradiation in acetonitrile to produce the spirocyclic enol ethers **194** or esters **196**. The ease of formation on the salts coupled with the exceptional chemical efficiencies and structural outcomes of these cyclizations indicates that this methodology will have synthetic utility. The results also demonstrate the importance of trialkylsilyl substituents in electron transfer photochemical studies both as mechanistic probes and as groups to control reaction efficiency and regiochemistry.



Acknowledgements—Financial support for the studies described in this report from our laboratory from the National Institutes of Health (GM-27251) and the National Science Foundation (CHE-09813) is acknowledged. Appreciation is expressed to the many competent and enthusiastic co-workers who have provided results through their research efforts which are incorporated in this report.

REFERENCES

[1] A. Padwa, *Chem. Rev.* **77**, 37 (1977).
[2] A. C. Pratt, *Chem. Soc. Rev.* **6**, 63 (1977).
[3] H. Bohme and H. G. Viehe, *Iminium Salts in Organic Chemistry*, Vol. 9. Wiley, New York (1976).
[4] P. A. Kollman, J. M. McKelvey and P. Gund, *J. Am. Chem. Soc.* **97**, 1640 (1975).

[5] P. A. Kollman, W. F. Trager, S. Rothenbert and J. E. Williams, *J. Am. Chem. Soc.* **95**, 458 (1973).
[6] J. M. Lehn, *Theor. Chim. Acta* **16**, 351 (1970).
[7] G. Olah and P. Kreienbuhl, *J. Am. Chem. Soc.* **89**, 4756 (1967).
[8] A. F. McDonagh and H. E. Smith, *J. Org. Chem.* **33**, 8 (1968).
[9] A. Krebs and J. Breckewoldt, *Tetrahedron Letters* 3797 (1969).
[10] A. Krebs, *Ibid.*1901 (1971).
[11] G. Opitz, H. Hellman and H. W. Schubert, *Liebigs Ann. Chem.* **623**, 117 (1959).
[12] H. Bohme and G. Anterhoff, *Chem. Ber.* **104**, 2013 (1971).
[13] J. R. Hargeaves, P. W. Hickmott anbd B. J. Hopkins, *J. Chem. Soc. C*, 2599 (1968).
[14] U. C. Yoon, S. L. Quillen, P. S. Mariano, R. Swanson, J. L. Stavinoha and E. Bay, *J. Am. Chem. Soc.* **105**, 1204 (1983).
[15] S. L. Murov, *Handbook of Photochemistry*. Marcel Dekker, New York (1973).
[16] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*. Academic Press, New York (1971).
[17] H. E. Zimmerman, K. S. Kamm and D. P. Werthemann, *J. Am. Chem. Soc.* **97**, 3718 (1975).
[18] D. Griller and F. P. Lossing, *J. Am. Chem. Soc.* **103**, 1586 (1981).
[19] A. Holy, J. Kupicka and Z. Arnold, *Coll. Czech. Chem. Commun.* **30**, 4127 (1965).
[20a] C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.* **26**, 223 (1970); [b] C. P. Andrieux and J. M. Saveant, *Bull. Soc. Chim. Fr.* 4671 (1968).
[21] C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.* **28**, 339 (1970).
[22] C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.* **28**, 446 (1970).
[23] K. Kano and T. Matsuo, *Tetrahedron Letters* 1389 (1975); K. Kano, T. Shibata, M. Kajiyara and T. Matsuo, *Tetrahedron Letters* 3693 (1975); L. Grossi, F. Minisci and G. F. Pedulli, *J. Chem. Soc. Perkin Trans.* **2**, 943 (1977); L. Grossi, F. Minisci and G. F. Pedulla, *J. Chem. Soc. Perkin Trans.* **2**, 1948 (1977).
[24] P. Hanson, *Adv. Heterocycl. Chem.* **25**, 205 (1980).
[25] E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.* **86**, 5515 (1964); E. M. Kosower and E. J. Poziomek, *Chem. Abstr.* **66**, 55399 (1967); E. M. Kosower and H. P. Waits, *Org. Prep. Proc. Int.* **3**, 261 (1971).
[26] G. A. Russell, R. Konalea, E. T. Strom, W. C. Danan, K. Y. Chang and G. Karupp, *J. Am. Chem. Soc.* **90**, 4646 (1968).
[27] M. Itoh and S. Nagakura, *Bull. Chem. Soc. Jap.* **39**, 369 (1966); H. Watanabe, Y. Ikegami and S. Seto, *Chem. Lett.* 1107 (1972); A. R. Katritzby and F. Soti, *J. Chem. Soc. Perkin Trans.* **1**, 1427 (1974).
[28] D. Guerin-Ouler, C. Nicollin, C. Siero and C. Lamy, *Mol. Phys.* **34**, 161 (1977).
[29] M. K. Polievktov, A. K. Sheinkman and L. N. Morozova, *Khim. Oerterotsikl Svedin.* 1067 (1973).
[30] E. Weitz, A. Roth and A. Nelken, *Ann. Chem.* **425**, 161 (1921).
[31] O. Dimroth and R. Heene, *Chem. Ber.* **54**, 2934 (1921).
[32] O. Dimroth and F. Fuster, *Chem. Ber.* **55**, 1223 (1922).
[33] A. T. Nielsen, D. W. Moore, G. M. Muhra and K. H. Berry, *J. Org. Chem.* **29**, 2175 (1964).
[34] E. R. Blout and R. S. Corley, *J. Am. Chem. Soc.* **69**, 763 (1947).
[35] G. F. Baumgartner, E. Gunther and G. Scheibe, *Z. Electrochem. Ber.* **60**, 570 (1956); G. Scheibe, *Chimia* **15**, 10 (1961).
[36] F. Dorr, J. Kotschy and H. Hansen, *Ber. Physik. Chem.* **69**, 11 (1965).
[37] W. Hoppe and F. Baumgartner, *Z. Kristallogr.* **108**, 328 (1957).
[38] G. Scheibe, J. Heiss and K. Feldmann, *Angew Chem. Int. Ed.* **4**, 525 (1965).
[39] H. H. Perkampus and B. Behjati, *J. Heterocycl. Chem.* **11**, 511 (1974).
[40] B. Behjati and T. Bluhm, *J. Heterocycl. Chem.* **16**, 1639 (1979).
[41] R. F. Childs and B. Dickie, *J. Chem. Soc.* Chem. Commun. 1268 (1981).
[42] B. Honig, *Ann. Rev. Phys., Chem.* **29**, 31 (1978).
[43] E. F. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.* **86**, 3094 (1964).
[44] G. M. Badger, C. P. Joshua and G. E. Lewis, *Tetrahedron Letters* 3711 (1964).
[45] G. M. Badger, R. S. Drewer and G. E. Lewis, *Austral. J. Chem.* **16**, 1042 (1963).
[46] E. C. Taylor, R. O. Kan and W. W. Paudler, *J. Am. Chem. Soc.* **83**, 4484 (1961).
[47] E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.* **85**, 776 (1963).
[48] E. C. Taylor, W. W. Paudler and I. Kuntz, *J. Am. Chem. Soc.* **83**, 2967 (1961).
[49] C. K. Bradsher and L. E. Beavers, *J. Org. Chem.* **22**, 1740 (1957).
[50] F. D. Greene, S. L. Misrock and J. R. Wolfe, *J. Am. Chem. Soc.* **77**, 3852 (1955).
[51] J. Bendig, B. Geppert and D. Kerysig, *J. Prakt. Chem.* **320**, 739 (1978).
[52] J. S. Swenten and J. A. Hyatt, *J. Am. Chem. Soc.* **96**, 4879 (1974); A. Howard and T. Koch, *J. Am. Chem. Soc.* **97**, 7288 (1975).
[53] J. L. Stavinoha and P. S. Mariano, *J. Am. Chem. Soc.* **103**, 3136 (1981).
[54] P. S. Mariano and A. Leone-Bay, *Tetrahedron Letters* 4581 (1980).
[55] K. E. Wilzbach, J. S. Ritscher and L. Kaplan, *J. Am. Chem. Soc.* **89**, 1031 (1967).
[56] L. Kaplan, J. W. Pavlik and K. E. Wilzbach, *J. Am. Chem. Soc.* **94**, 3283 (1972).
[57] K. Takagi and Y. Ogata, *J. Chem. Soc. Perkin Trans* **2**, 1402 (1979).
[58] U. C. Yoon, S. L. Quillen, P. S. Mariano, R. Swanson, J. L. Stavinoha and E. Bay, *Tetrahedron Letters* 919 (1982).
[59] T. Forster and K. Kasper, *Z. Phys. Chem.* **1**, 275 (1954); J. B. Birks, *Prog. Reaction Kinetics* **5**, 181 (1970); T. Forster, *Angew. Chem. I.E.* **8**, 333 (1969); B. Stevens and E. Hutton, *Nature*, **186**, 1045 (1960); M. S. Walker, T. W. Bednar and R. Lumry, *J. Chem. Phys.* **45**, 3455 (1966); R. Hochstrasser, *J. Chem. Phys.* **36**, 1099 (1962); H. Leonhardt and A. Weller, *Ber. Bunsenges. Physik. Chemie.* **67**, 791 (1963).
[60] T. Forster, K. Kasper, *Z. Electrochem.* **59**, 976 (1955).
[61] J. Ferguson, *J. Chem. Phys.* **28**, 765 (1958).
[62] H. Knibbe, D. Rehm and D. Weller, *Z. Phys. Chem.* **56**, 95 (1967).
[63] H. Knibbe, D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.* **72**, 257 (1968); W. R. Ware and H. P. Richter, *J. Chem. Phys.* **48**, 1595 (1968).
[64] A. E. W. Knight and B. K. Selinger, *Chem. Phys. Lett.* **10**, 43 (1971).
[65a] H. Beens and A. Weller, *Chem. Phys. Lett.* **2**, 140 (1968); [b] D. Rehm and A. Weller, *Isr. J. Chem.* **8**, 259 (1970).
[66] M. T. Indelli and F. Scandola, *J. Am. Chem. Soc.* **100**, 7733 (1978); F. Scandola and V. Balzani, *J. Am. Chem. Soc.* **101**, 6140 (1979); F. Scandola, V. Balzani and G. B. Schuster, *J. Am. Chem. Soc.*, **103**, 2519 (1981).
[67] H. Knibbe, K. Rollig, F. P. Schofer and A. Weller, *J. Chem. Phys.* **47**, 1184 (1967).

[68] K. Kawai, N. Yamamoto and H. Tsubomura, *Bull. Chem. Soc. Jap.*, **42**, 369 (1969); Y. Nakato, N. Yamamoto and H. Tsubomura, *Bull. Chem. Soc. Jap.* **40**, 2480 (1967); E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.* **9**, 393, 397 (1971); D. R. G. Brimage, R. S. Davidson, *J. Chem. Soc.* Chem. Commun. 1385 (1971); K. Ide, Y. Sakata, S. Misumi, T. Okada and M. Mataga, *J. Chem. Soc.* Chem. Commun. 1009 (1972).

[69] N. J. Turro, *Modern Molecular Photochemistry*, Benjamin, New York (1978).

[70] See for example Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc.* Chem. Commun. 407 (1975); A. J. Maroulis, Y. Shigemitsu and D. R. Arnold, *J. Am. Chem. Soc.* **100**, 535 (1978); V. R. Rao and S. S. Hixson, *J. Am. Chem. Soc.* **101**, 6458 (1979); T. Majima, C. Pac and H. Sakurai, *J. Am. Chem. Soc.* **102**, 5265 (1980).

[71] F. W. McLafferty, *Interp. of Mass. Spec.* 3rd Edn. University Science Books, California (1980).

[72] C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Non-Aqueous Systems.* Marcel Kekker, New York (1970).

[73] P. S. Mariano, J. Stavinoha and E. Bay, *Tetrahedron* **37**, 3385 (1981).

[74] E. LaGoff and R. B. LaCount, *J. Am. Chem. Soc.* **85**, 1354 (1963).

[75] J. Nasielski and E. Vanderdonckt, *Theor. Chim. Acta.* **2**, 22 (1964).

[76] E. M. Kosower and J. Skorcz, *J. Am. Chem. Soc.* **82**, 2195 (1960).

[77] E. M. Kosower, *J. Am. Chem. Soc.* **80**, 3253 (1958).

[78] B. G. White, *Farad. Soc. Trans.* **65**, 2000 (1965).

[79] A. Ledwith and H. J. Woods, *J. Chem. Soc. C* 1422 (1970).

[80] E. M. Kosower and L. Lindquist, *Tetrahedron Letters* 4481 (1965).

[81] R. F. Cozzens and T. A. Gover, *J. Phys. Chem.* **74**, 3003 (1970).

[82] P. Slade, *Nature* **207**, 515 (1965).

[83] J. F. McKellar and P. H. Turner, *Photochem. Photobiol.* **13**, 437 (1971).

[84] J. R. Barnett, A. S. Hopkins and A. Ledwith, *J. Chem. Soc. Perkin* **2**, 80 (1973).

[85] H. D. Burrows, D. Greatorex and T. T. Kemp, *J. Am. Chem. Soc.*, **93**, 2539 (1971).

[86] E. Vogelmann, W. Rauscher and H. E. A. Kramer, *Photochem. Photobiol.* **29**, 771 (1979).

[87] T. G. Beaumont K. M. C. Davis, *J. Chem. Soc. B* 456 (1970).

[88] A. Castellano, J. P. Catteau and A. Lablanche-Combier, *Tetrahedron* **31**, 2255 (1975).

[89] C. Chachaty, J. C. Ronford-Haret, A. Lablanche-Combier, T. P. Qugeleur and H. Offenberg, *J. Chem. Soc.* Chem. Commun. 579 (1974).

[90] F. D. Saeva and G. R. Olin, *J. Chem. Soc.* Chem. Commun. 401 (1980).

[91a] I. Willner, J. W. Otuos and M. Calvin, *J. Am. Chem. Soc.* **103**, 3203 (1981); [b] J. S. Bellin, R. Alexander and R. D. Mahoney, *Photochem. Photobiol.* **17**, 17 (1973).

[92a] P. Hyde and A. Ledwith, *J. Chem. Soc. Perkin II* 1768 (1974); [b] B. M. Vittimberga, F. Minisci and S. Morrocchi, *J. Am. Chem. Soc.* **97**, 4397 (1975).

[93] D. G. Whitten, *The Photochemistry of Heterocyclic Compounds* (Edited by O. Buchard), p. 524. Wiley, New York (1976).

[94] A. Ledwith, *Acc. Chem. Res.* **5**, 133 (1972).

[95] J. A. Farrington, A. Ledwith and M. F. Stam, *J. Chem. Soc.* Chem. Commun. 259 (1969).

[96] C. S. Johnson and H. S. Gutowsky, *J. Chem. Phys.* **39**, 58 (1963).

[97] A. S. Hopkins, A. Ledwith and M. F. Stam, *J. Chem. Soc.* Chem. Commun. 494 (1970).

[98] A. Ledwith, P. J. Russell and L. H. Satcliffe, *J. Chem. Soc.* Chem. Commun. 964 (1971).

[99] A. Ledwith, P. J. Russell and L. H. Satcliffe, *Proc. Roy. Soc.* **332**, 151 (1973).

[100] E. G. Janzen, *Acc. Chem. Res.* **4**, 31 (1971); E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.* **91**, 4481 (1969).

[101] D. H. Ellison, G. A. Salman and F. Wilkinson, *Proc. Roy. Soc. A* **328**, 23 (1972).

[102] F. S. Dainten, I. V. Janovsky and G. A. Salman, *J. Chem. Soc.* Chem. Commun. 335 (1969).

[103] M. A. T. Rodgers, *Photochem. Photobiol.* **29**, 1031 (1979).

[104] N. M. D. Brown, D. J. Cowley and W. J. Murphy, *J. Chem. Soc.* Chem. Commun. 592 (1973).

[105] N. M. D. Brown, D. J. Cowley and M. Hashimi, *J. Chem. Soc., Perkin Trans* **2**, 462 (1979).

[106] A. S. Hopkins and A. Ledwith, *J. Chem. Soc.* Chem. Commun. 830 (1971).

[107a] T. J. VanBergen and R. M. Kellogg, *J. Am. Chem. Soc.* **94**, 8451 (1972); [b] T. Furihata, A. Sugimori, *J. Chem. Soc.* Chem. Commun. 241 (1975); [c] F. R. Stermitz, R. P. Seiber and D. E. Nicodem, *J. Org. Chem.* **33**, 1136 (1968).

[108] F. R. Stermitz, R. Pua and H. Vyas, *J. Chem. Soc.* Chem. Commun. 326 (1967).

[109] F. R. Stermitz, R. P. Seiber and D. E. Nicodem, *J. Org. Chem.* **33**, 1136 (1968).

[110] F. R. Stermitz, C. C. Wei and W. H. Huang, *J. Chem. Soc.* Chem. Commun. 482 (1968).

[111] E. F. Travecedo and V. I. Stenberg, *J. Chem. Soc.* Chem. Commun. 609 (1970).

[112] F. Takeuchi, T. Sugigama, T. Fujimori, K. Seki, Y. Horada and A. Sugimori, *Bull. Chem. Soc. Jap* **47**, 1245 (1974).

[113] M. Ochiai and K. Morita, *Tetrahedron Letters* 2349 (1967).

[114] E. C. Taylor, Y. Maki and B. E. Evans, *J. Am. Chem. Soc.* **91**, 5181 (1969).

[115] M. Ochiai, E. Mizata, Y. Asahi and K. Morita, *Tetrahedron* **24**, 5870 (1968).

[116] S. Wake, Y. Takayama, Y. Otsuji and E. Imoto, *Bull. Chem. Soc. Jap.* **47**, 1257 (1974).

[117] J. W. Happ, M. T. McCall and D. G. Whitten, *J. Am. Chem. Soc.* **93**, 5496 (1971).

[118] M. J. McCall and D. G. Whitten, *J. Am. Chem. Soc.* **91**, 6581 (1969).

[119] J. W. Hap, J. A. Ferguson and D. G. Whitten, *J. Org. Chem.* 1485 (1972).

[120] S. Wake, H. Inoue, Y. Otsuji and E. Imoto, *Tetrahedron* **28**, 2415 (1970).

[121] S. Wake, Y. Otsuji and E. Imoto, *Bull. Soc. Chem. Jap.* **47**, 1251 (1974).

[122] D. N. Bailey, D. K. Roe and D. M. Hercules, *J. Am. Chem. Soc.* **90**, 6291 (1968).

[123] S. W. Wang, *Biochemistry* **7**, 3740 (1968).

[124] J. Joussot-Dubien and J. Houdard-Pereyre, *Bull. Soc. Chim. Fr.* **8**, 2619 (1969).

[125] V. V. Zanker and H. Cnobloch, *Z. Naturforschg* **17b**, 819 (1962).

[126] V. V. Zanker, E. Erhardt, F. Mader and J. Thies, *Z. Naturforschg.* **21b**, 102 (1966).

[127] A. Castellano, J. P. Catteau, A. Lablache-Combier and B. Timland, *J. Chem. Res.* **(s)**, 170 (1979).

[128] H. Inoue, T. Sakurai and F. Tanaka, *Bull. Chem. Soc. Jap.* **48**, 924 (1975).

[129] H. Inoue, Y. Hiroshima and N. Makiga, *Bull. Chem. Soc. Jap.* **52**, 351 (1979).

[130] K. Wallenfels and M. Gellrich, *Chem. Ber.* **92**, 1406 (1959).

[131] D. Mauzerall and F. H. Westhermir, *J. Am. Chem. Soc.* **77**, 77 (1955).

[132] J. N. Burnett and A. L. Underwood, *J. Org. Chem.* **30**, 1154 (1965); *Biochem.* **6**, 266 (1967).

[133] K. Wellenfels and H. Schultz, *Angew. Chem.* **67**, 517 (1955).

[134] R. A. Krasnovski and G. P. Brin, *Dokl. Acad. Nauk. USSR* **67**, 325 (1949).

[135] G. R. Seely, *J. Phys. Chem.* **69**, 2779 (1965).

[136] T. T. Banister and J. E. Bernardine, *Biochem. Biophys. Acta.* **59**, 188 (1962).

[137] L. P. Vernon, A. S. Pietro and D. A. Limbach, *Arch. Biochem. Biophys.* **109**, 92 (1965).

[138] T. Matsurra, T. Itahara, T. Otsuki and I. Saito, *Bull. Chem. Soc. Jap.* **51**, 2698 (1978).

[139] K. Kano and T. Matsuo, *Tetrahedron Letters* 1389 (1975).

[140] K. Kano and T. Matsuo, *Bull. Soc. Chem. Jap.* **49**, 3269 (1976).

[141] K. Kano, T. Shibata, M. Kajiyara and T. Matsuo, *Tetrahedron Letters* 3693 (1975).

[142] V. Stenberg and E. F. Travecedo, *Tetrahedron* **27**, 513 (1971).

[143] Y. Ogata, K. Takugi and Y. Tanabe, *J. Chem. Soc., Perkin Trans.* **2**, 1069 (1979).

[144] H. Nozaki, M. Kato R. Noyori and M. Kawanisi, *Tetrahedron Letters* 4259 (1967).

[145] R. Noyori, M. Kato, M. Kawanisi and H. Nozaki, *Tetrahedron* **25**, 1125 (1969).

[146] S. Futamura, H. Ohta and Y. Kamiya, *Tetrahedron Letters* 4299 (1979).

[147] P. S. Mariano, J. L. Stavinoha, G. Pepe and E. F. Meyer, *J. Am. Chem. Soc.* **100**, 7114 (1978).

[148] P. S. Mariano, J. L. Stavinoha and R. Swanson, *J. Am. Chem. Soc.* **99**, 6781 (1977).

[149] J. L. Stavinoha, P. S. Mariano, A. Leone-Bay, R. Swanson and C. Bracken, *J. Am. Chem. Soc.* **103**, 3148 (1981).

[150] T. Tiner-Harding, J. W. Ullrich, F. T. Chiu, S. F. Chen and P. S. Mariano, *J. Org. Chem.* **47**, 3360 (1982).

[151] Unpublished results of S. L. Quillen, A. Lan, R. Heuckeroth, L. Klingler and P. S. Mariano.

[152] S. G. Cohen, A. H. Parola and G. H. Parsons, *Chem. Rev.* 141 (1973); S. Inbar, H. Linschitz and S. Cohen, *J. Am. Chem. Soc.* **103**, 1048 (1981).

[153] D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.* **98**, 5931 (1976).

[154] R. S. Davidson and P. R. Steiner, *J. Chem. Soc. Perkin II* 1357 (1972); R. S. Davidson, S. P. Orton, *J. Chem. Soc.* Chem. Commun. 209 (1974).

[155] R. S. Davidson and P. R. Steiner, *J. Chem. Soc. C.* 1682 (1975); D. R. G. Brimage, R. S. Davidson and P. R. Steiner, *J. Chem. Soc. Perkin I* 526 (1973); D. R. G. Brimage and R. S. Davidson, *J. Chem. Soc. Perkin I* 496 (1973).

[156a] H. Goth, P. Cerrutti and H. Schmid, *Helv. Chim. Acta* **50**, 1759 (1967); P. Cerrutti and H. Schmid, *Helv. Chim. Acta* **47**, 203; 1962 (1964) [b] R. Gault and A. I. Meyers, *J. Chem. Soc.* Chem. Commun. 778 (1971).

[157] J. L. Stavinoha, E. Bay, A. Leone and P. S. Mariano, *Tetrahedron Letters* 3455 (1980); P. S. Mariano, J. L. Stavinoha and E. Bay, *Tetrahedron* **37**, 3385 (1981).

[158] H. D. Roth, M. Manion-Schilling and G. Jones, *J. Am. Chem. Soc.* **103**, 1246 (1981); Albini-A. and D. R. Arnold, *Can. J. Chem.* **56**, 2985 (1978); P. G. Gassman, K. D. Olson, L. Walter and R. Yamaguchi, *J. Am. Chem. Soc.* **103**, 4977 (1981).

[159] K. Ohga and P. S. Mariano, *J. Am. Chem. Soc.* **104**, 617 (1982).